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An overview of biodiesel oxidation stability

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ABSTRACT

Oxidation Stability is one of the most important properties of fatty acid alkyl esters (biodiesel fuel) and primarily affects the stability of biodiesel during extended storage. Degradation by oxidation yields products that may compromise fuel properties, impair fuel quality and engine performance. In Europe, standardization and fuel quality assurance are crucial factors for biodiesel market acceptance, and storage stability is one of the main quality criteria. An overview of researches into biodiesel oxidation stability is presented in an attempt to convey the significance of this important property of biodiesel fuel. Aspects covered include: significance of biodiesel oxidation stability, oxidation chemistry, methods used for characterization of stability, factors known to influence stability, and consequences of biodiesel oxidation for diesel engines. The purpose of this work was to review the findings from some of the key prior research efforts available in the literature and to identify aspects of biodiesel oxidation stability in need of further study.

Contents

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1. Introduction

“Fuel stability” is the resistance of a fuel to degradation processes that can change fuel properties and form undesirable species. A fuel is considered unstable when it readily undergoes these changes. Biodiesel fuel properties can degrade by one or more of the following mechanisms: (i) oxidation or autoxidation from contact with oxygen present in ambient air; (ii) thermal or thermal-oxidative decomposition from excess heat; (iii) hydrolysis from contact with water or moisture in tanks and fuel lines; or (iv) microbial contamination from migration of dust particles or water droplets containing bacteria or fungi into the fuel [1].

“Oxidation stability” refers to the tendency of fuels to react with oxygen at temperatures nearer ambient—mechanism (i) and describes the relative susceptibility of the fuel to degradation by oxidation. These reactions are much slower than those that would occur at higher temperatures. The degree of oxidative degradation suffered by biodiesel prior to combustion in a diesel engine, will be affected by a multitude of factors including the nature of the original lipid feedstock, biodiesel production method, fuel additives and impurities, storage and handling conditions, as well as by conditions within the fuel tank and fuel delivery system.

“Thermal stability” addresses susceptibility to degradation due to greatly elevated temperatures, much higher than ambient—mechanism (ii) and is relevant to biodiesel usage since high fuel temperatures may occur at conditions encountered in engine fuel injection systems, as fuel is re-circulated through the injection system and back to the fuel tank.

“Storage stability” is a frequently used term and refers to the general stability of the fuel while it is in long-term storage. Oxidative degradation is probably one of the primary concerns of storage stability but storage stability might also involve issues of water contamination and microbial growth [2]. Water can promote microbial growth, lead to tank corrosion, participate in the formation of emulsions, as well as cause hydrolysis or hydrolytic oxidation [3]. Microbiological stability of biodiesel and petro-diesel mixtures was discussed in detail by Schleicher et al. [4], and this topic is not described any further here. The term “oxidation stability” is more general and is distinguished from the term “storage stability” since oxidation may occur not only during storage but also during production and end-use [5]. The aim of this work is to review some of the key previous researches into biodiesel oxidation stability and identify aspects in need of further investigation.

1.1. The significance of biodiesel oxidation stability

Oxidation stability is one of the most important properties of fatty-acid methyl esters [6] and affects biodiesel primarily during extended storage [7]. Biodiesel tends to be less resistant to oxidation than petroleum diesel [8]. Degradation by oxidation yields oxidation products that may compromise fuel properties, impair fuel quality and engine performance, thus oxidation stability is an important issue that biodiesel research must address [3]. Companies that transport and store biodiesel are concerned that biodiesel may form sediment during storage. Vehicle and equipment operators need assurances that sediment and gums will not form in equipment during use [9]. For the Fuel Injection Equipment (FIE) manufacturers a key property of any FAME fuel is the resistance to oxidation. Aged or poor quality FAME contains products which can drastically reduce the service life of the FIE [10].

In recent times the commercial production levels of biodiesel in the European Union have grown rapidly. Standardization and fuel quality assurance are crucial factors for market acceptance, and storage stability is one of the main quality criteria [3,11]. Fuels not meeting the same quality standard results in a high degree of variability in fuel properties and subsequent engine performance. A rigorous fuel quality standard is necessary if any manufacturer is to extend warranty coverage to biodiesel fueled engines. Specifications related to oxidation stability have accordingly been included in European EN 14214 and American ASTM D6751 biodiesel standards, since diesel engine performance and maintenance problems can arise due to oxidative degradation of biodiesel, particularly in the engine fuel system. Oxidative degradation of biodiesel can lead to the formation of, acids, insoluble

sediments, and varnish deposits. Fuel properties may significantly alter. Insoluble materials can clog engine fuel lines and filters. Corrosive and or deposit forming species can affect the deterioration of engine parts and lead to operating problems. Although biodiesel degradation due to oxidative instability is thus a disadvantage, it can also be advantageous in environmental terms, since it means biodiesel is more readily biodegradable relative to petro-diesel [12].

1.1.1. Deposits and corrosion

When biodiesel is oxidized, the resulting sediments can negatively influence the performance of the fuel system [8]. One potential problem is tendency to form deposits on engine parts such as injectors and critical fuel pump components [13]. In some cases, oxidation results in the chemical structure of biodiesel breaking apart to form shorter chain acids and aldehydes. In its advanced stages, oxidation causes biodiesel to become acidic, causing fuel system corrosion [14]. Corrosive acids and deposits may cause increased wear in engine fuel pumps and injectors [6]. Water present in the fuel can cause the formation of rust and corrosion exacerbated by the presence of acids and hydroperoxides formed by fuel oxidation [15].

1.1.2. Insoluble polymers

Product species of oxidation can cause polymerization-type reactions to produce high molecular weight insoluble sediments and gums. The most likely impact of sediment and gum formation will be fuel filter plugging and varnish deposition on fuel system components; and these phenomena have been observed [14]. Polymerization-type reactions lead to the formation of higher molecular weight products and an increase in viscosity. Insoluble species formation can clog fuel lines and pumps. It has been reported that polymers formed can be soluble in biodiesel, and yet become insoluble when mixing the biodiesel with petro-diesel [16]. Thus at very high levels of oxidation, biodiesel blends with petro-diesel can separate into two phases causing fuel pump and injector operational problems.

1.1.3. Degradation of elastomers

Unstable oxidation products have a tendency to attack elastomers [14]. Oxidation of biodiesel leads to the formation of hydroperoxides, which can attack elastomers or polymerize to form insoluble gums. Oxidation products such as hydroperoxides and carboxylic acids can act as plasticizers of elastomers [15].

1.1.4. Fuel properties

Flash point as well as other fuel properties can also change due to oxidative instability [15]; potentially raising issues beyond the fuel delivery system. Fuel chemistry changes caused by oxidation can produce significant changes in engine performance and emissions. Oxidation affects several fuel properties including viscosity and Cetane number. If these changes are significant and deleterious, they could cause engines using oxidized fuel to no longer meet manufacturer performance goals or government regulations for emissions certification [14]. The exhaust emissions of a diesel engine operating on biodiesel are influenced by oxidation of the biodiesel [5]. Further, biodiesel may contaminate engine lubricating oil where polymerization-type reactions can occur, forming sludge and increasing engine wear [17]. Biodiesel can affect a loss of oxidation stability of the lube oil [15]. Altered lubricant properties may further impact related components such as bearings, seals, hoses, oil passages and filters.

Previous engine performance and durability studies described by Knothe et al. [18] showed that combustion of neat (100%) vegetable oils and their blends with petro-diesel lead to incomplete combustion, injector nozzle coking, engine deposits, piston ring sticking and contamination of crankcase lubricant. Contamination and polymerization of lubricating oil lead to an increase in lubricant viscosity. Many problems were traced to poor fuel atomization aggravated by the high viscosity of vegetable oils (typically an order of magnitude greater than petro-diesel). It is likely that highly oxidized, higher viscosity biodiesel could present similar problems. Some fuel quality complaints have been reported after using biodiesel; often due to fuel filter plugging and injector fouling and some about hard starting [8], though causes are not always pinpointed.

Bannister et al. [19] noted oxidation of biodiesel leads to a change in fuel colour from yellow to brown, accompanied by a pungent vinegary smell, as well as a reduction in heating value, an increase in Cetane number, viscosity, acid value, and the formation of polymers that can block fuel filters and injectors.

1.2. Summary of oxidation chemistry

Oxidation and thermal instability can result in the degradation of biodiesel fuel properties and deleteriously affect engine performance. Instability is fundamentally a consequence of fatty acid chain unsaturation (carbon double bonds C=C). Both of these instability types are determined by the amount and configuration of fatty acid chain unsaturation [13]. Instability is greatly exacerbated if two or more carbon double bonds are present in the fatty acid chain [15], so that more highly unsaturated fatty acid chains are relatively less stable. In the process of oxidative degradation, unsaturated sites of a fatty acid chain undergo free radical attack; where a hydrogen atom is abstracted from the fatty acid chain. Ambient oxygen then readily reacts at the site, subsequently forming hydroperoxide. This oxidation process is a self-sustaining chain reaction that proceeds slowly at first, and then suddenly much more rapidly after an initial ‘induction period’ has elapsed. Once formed, hydroperoxides accumulate and then later decompose, inter-reacting to form numerous problematic secondary oxidation products, including aldehydes, alcohols, short chain carboxylic acids, and higher molecular weight oligomers. Therefore oxidation affects an increase of insoluble sediments, acidity and viscosity [9].

In thermal instability, the unsaturated sites of one fatty acid chain can react with those of another fatty acid chain at sufficiently high temperature, forming polymers (dimers and trimers). Thermal polymerization of esters only becomes important when temperatures of 250–300 °C are reached [13]. Biodiesel tends to be very thermally stable but less oxidatively stable when compared to petroleum diesel [6]—not surprising, being derived from vegetable oils that are known to be well suited to high temperature cooking applications. Thermal polymerization occurs by the Diels Alder reaction; where two fatty acid chains become linked by a cyclohexane ring. Higher oligomers are possible but their exact formation mechanism is not established [13].

FAME comprises fatty acid chains esterified to methanol. Scientists have been investigating the oxidation process of unsaturated fatty acid chains found in fatty oils and their esters for several decades; the oxidation process is known as ‘‘autoxidation’’ or ‘‘peroxidation’’, as discussed by Frankel [20]. Understanding of fatty oils and esters chemistry is thus reasonably mature.

1.2.1. Chemical structure of fatty acid chains

Polyunsaturated fatty acid chains commonly found in many plant-derived oils contain allylic and bis-allylic sites, which are methylene interrupted chains, and these are crucial to understanding instability. In most naturally occurring Triacylglycerides (TAG) feedstocks, multiple fatty acid chain unsaturation occurs in

a methylene-interrupted configuration, as depicted below for linolenic acid. Double bonds are shown located at carbons 9, 12, and 15 along the chain, with methylene (**CH_2**) groups interrupting the double bonds.

$HOOC–(CH_2)_7–CH=CH–\mathbf{CH_2}–CH=CH–\mathbf{CH_2}–CH=CH–CH_2–CH_3$ (methylene interupted)

An isomer of linolenic acid, having a conjugated arrangement of unsaturation is shown below.

$HOOC–(CH_2)_7–CH=CH–CH=CH–CH=CH–(CH_2)_3–CH_3$ (conjugated)

The conjugated arrangement of unsaturation is the most thermodynamically stable arrangement, though rearrangement from methylene interrupted to conjugated configuration does not occur at ordinary temperatures, due to the necessarily high activation energy required to break and reform bonds [13].

Autoxidation proceeds at different rates depending on the number and position of double bonds. Allylic sites are especially susceptible to oxidation and bis-allylic sites even more so. An allylic site is a methylene CH_2 adjacent only to one double bond. A methylene CH_2 group located between two double bonds is a bis-allylic site; being twice allylic to a double bond in the fatty acid chain structure. Linoleic acid has double bonds at Δ9 and Δ12 giving one bis-allylic site at C-11.

Linoleic acid: $HOOC–(CH_2)_7–CH=CH–CH_2–CH=CH–(CH_2)_4–CH_3$

Linolenic acid (above) has double bonds at Δ9, Δ12 and Δ15; giving two bis-allylic sites: one at C-11 and the other at C-14. Relative rates of oxidation for the different fatty structures were reported by Knothe and Dunn [5] to be: 1 for oleates, 41 for linoleates, and 98 for linolenates. Most biodiesel fuels contain significant amounts of esters of oleic, linoleic or linolenic acids; influencing the oxidation stability of the fuel. Small amounts of more highly unsaturated fatty compounds have a disproportionately strong effect in reducing oxidation stability [7].

1.2.2. Primary oxidation

The general mechanism by which oxidation of unsaturated fatty acids proceeds is by classical free radical chain reaction steps; initially forming the peroxides that go on to degrade by a number of pathways to secondary oxidation products, such as acids, aldehydes, dimers and polymers [9]. The chain reaction proceeds by the three steps: initiation, propagation and termination. Reactions can be sequential and overlapping. General examples of these reactions are as follows:

Step 1: Initiation

$$RH + I\cdot \rightarrow R\cdot + IH \quad (1)$$

Initiator radicals ($I\cdot$) react with the fatty acid substrate (RH) removing hydrogen from a carbon atom of the fatty acid chain, to form a new carbon-based fatty acid radical ($R\cdot$). Initiator radicals ($I\cdot$) are formed by various different mechanisms [20], including:

i. Thermal dissociation of hydroperoxides (ROOH) present as impurities

$$ROOH \rightarrow RO^{\bullet} + OH^{\bullet} \quad (2)$$

ii. Metal (M) catalysed decomposition of hydroperoxides

$$ROOH + M^{2+} \rightarrow RO^{\bullet} + OH^{\bullet} + M^{3+} \quad (3)$$

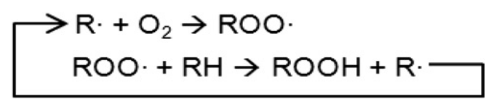
$$ROOH + M^{3+} \rightarrow ROO^{\bullet} + H^{+} + M^{2+} \quad (4)$$

iii. Oxidation can also be catalysed by exposure to light, a process called "photo-oxidation".

The initiation process is most likely to be the metal-catalysed reaction of hydroperoxides since trace metals that act as potent catalysts are very difficult to eliminate [20]. Photo-oxidation requires exposure to ultraviolet light and the presence of a photo sensitizer, and is unlikely to be significant factor in biodiesel degradation [21], since fuel should be kept in opaque fuel tanks and containers.

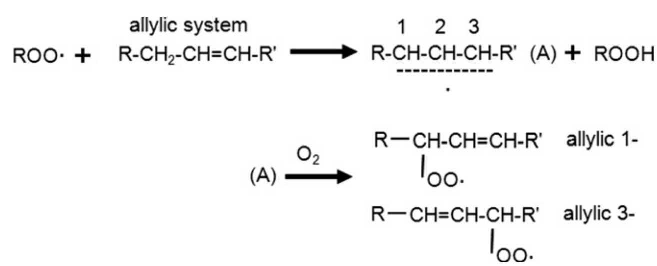
Step 2: Propagation

The fatty acid radical ($R^{\bullet}$) that is initiated, proceeds to readily react with molecular oxygen to form a fatty acid peroxide radical ($ROO^{\bullet}$), which is unstable and goes on to react with the original substrate RH, abstracting hydrogen, to form a fatty acid hydroperoxide (ROOH) as well as a further new fatty acid radical ($R^{\bullet}$). These events are the basis of a radical chain-reaction as shown in Eq. (5), whereby the new fatty acid radical ($R^{\bullet}$), again reacts with oxygen, resulting in a self-sustaining chain reaction and an accumulation of fatty acid hydroperoxide (ROOH).



(5)

This is the most widely occurring oxidation reaction; forming hydroperoxides as the fundamental primary product of oxidation. The hydroperoxide forming reaction determines the rate of oxidation. The availability of relatively weakly bound allylic hydrogens in the fatty acid chain, and the relative ease with which they react with peroxyl radicals ($ROO^{\bullet}$), determines the degree of susceptibility to autoxidation. Peroxyl radical ($ROO^{\bullet}$) reacts with the allylic system as shown in Eq. (6), producing a hybrid radical intermediate (A). Oxygen attack at each end of the allylic system produces a mixture of allylic 1- and 3-hydroperoxides, as described in detail by Frankel [20]:



(6)

Step 3: Termination

In the termination step, the chain reaction ends when two free radicals meet and react to produce a non-radical species—see Eqs. (7) and (8).

$$R^{\bullet} + R^{\bullet} \rightarrow R–R \quad (7)$$

$$ROO^{\bullet} + ROO^{\bullet} \rightarrow \text{stable products} \quad (8)$$

This happens only when the concentration of radical species is sufficient for there to be a high probability of two radicals actually colliding [22]. At low temperatures, peroxyl radicals ($ROO^{\bullet}$) can combine to produce peroxyl linked molecules (R–OO–R), liberating oxygen—see Eq. (9):

$$ROO + ROO \rightarrow R–OO–R + O_2 \quad (9)$$

During the initial period of oxidation the ROOH concentration remains very low until an interval of time has elapsed. This period of time is often referred to as the "induction period (IP)", which is

determined by the relative susceptibility to oxidation (oxidation stability) of the TAG or alkyl ester, and according to the conditions under which it is stressed (temperature, oxygen exposure). Once the IP has elapsed, the ROOH level quickly increases, signalling the onset of rapid oxidation [13].

In the 3-step chain reaction described above, the most easily abstracted hydrogens are those bonded to carbons allylic to unsaturated sites of the fatty acid chain. Carbons that are simultaneously allylic to two unsaturated sites (bis-allylic sites) will be extremely susceptible to hydrogen abstraction. The carbons at bis-allylic sites are the sites of first attack. The bis-allylic methylene groups that interrupt multiple carbon double bonds in fatty acid chains are very susceptible to the initiation of peroxidation [13].

More highly unsaturated fatty acid chains are hence more prone to oxidation. Relative rates of oxidation correspondingly increase with the degree of unsaturation for methyl esters of oleic (18:1), linoleic (18:2) and linolenic (18:3) acids. Previous work discussed by Waynick [13] has shown the rate of oxidation to be proportional to the number of bis-allylic carbons present—the work reportedly examined pure unsaturated fatty acids, with oxidation rate measured by oxygen consumption in a closed system [13]. Consequently, as linoleic (18:2) and linolenic (18:3) acid content in TAG or alkyl esters increases, susceptibility to oxidation increases. Methods that reduce fatty acid chain unsaturation, such as fractional crystallization or hydrogenation are effective at greatly increasing oxidation stability. Falk and Meyer-Pittroff [23] demonstrated that the oxidation stability of FAME can be improved by performing distillation fractionation to remove FAME with shorter chain lengths ($\leq$C16) followed by partial hydrogenation of the remaining ($\geq$C18) fraction. However, these methods are usually unsuitable for application to biodiesel due to added cost, complexity and resulting conflict with other important fuel properties—for example, hydrogenation worsens cold flow properties.

1.2.3. Oxidation progression

As oxidation progresses, hydroperoxide (ROOH) levels can either increase and plateau at a steady state value, or can achieve a peak and then decrease [13]. The reasons for the two distinct behaviours are said not to be completely clear, though a host of factors such as oxygen availability, temperature, extent of previous oxidation, and presence of metal catalysts are likely involved [13]. Though clearly, if oxygen is not sufficiently abundant ROOH formation can slow or even stop, while ROOH decomposition continues—causing a peak in ROOH concentration. Similarly, other factors that increase ROOH decomposition rate can cause ROOH concentration to peak (factors such as higher temperature or increased presence of hydroperoxide decomposing metal catalysts, like copper and iron). Regardless of ROOH concentration profile (peak or no), maximum ROOH levels formed are typically 300–400 meq O_2/kg [13], although higher ROOH levels have been observed.

1.2.4. Secondary oxidation products

Once formed, hydroperoxides (ROOH) proceed to decompose and inter-react to form numerous secondary oxidation products including aldehydes, alcohols, short chain carboxylic acids, and higher molecular weight oligomers, even at ambient temperature [9]. Specific secondary products that can be formed include:

- Aldehydes (hexenals, heptenals, propane, pentane, and 2,4-heptadienal have also been detected). One study detected 25 different aldehydes during vegetable oil oxidation [13].
- Aliphatic alcohols
- Formate esters
- Shorter chain fatty acids, such as formic acid. The mechanism of decomposition of hydroperoxides to formic acid has been explained by Hasenhuettle [24].
- Polymeric species formed by linking of fatty acid chains. These rarely become larger than trimers or tetramers [13] though the reason for this is not apparent in the open literature. Polymer formation will increase viscosity. Fatty acids are joined by C–O–C and C–C linkages.

The mechanism of "vinyl polymerization" has also been proposed to be responsible for polymer formation, though conventional understanding of oxidation chemistry implies this mechanism would not be significant when oxygen was abundant—the importance of the mechanism in terms of biodiesel degradation has not been determined [13].

1.3. Antioxidants

Antioxidants act to inhibit the oxidation process and are well established for use to control oxidation of biodiesel. There are two types: chain breakers and hydroperoxide decomposers. Openly reported biodiesel development work has been entirely limited to the chain breaking type; the two common types are phenolic and amine, of which almost all fatty oil and ester work has been limited to phenolic-types [13]. The general mechanism by which all chain breaking types (A) work is shown in Eq. (10) below:

$$\mathrm{ROO}\bullet + \mathrm{AH} \rightarrow \mathrm{ROOH}\bullet + \mathrm{A}\bullet$$
$$\mathrm{A}\bullet \rightarrow \text{stable products} \tag{10}$$

The antioxidant (AH) intercepts the peroxide radical ($ROO^\bullet$); preventing it from creating another radical by the autoxidation mechanism. The antioxidant contains a more easily abstracted hydrogen, compared to that of a fatty oil or ester. The antioxidant free radical is either stable or further reacts to form a stable molecule that does not contribute to the oxidation process. The oxidation chain reaction is thus interrupted, while the antioxidant is consumed. Hydroperoxide decomposer antioxidants work by reacting with hydroperoxides and converting them to alcohols, while the antioxidant is changed to an innocuous oxidized form.

In fatty oils and their esters, antioxidants can be present naturally (present in the parent oil), or can be added deliberately. Natural and synthetic types are available as additives which can improve the stability of biodiesel. Tocopherols are such natural antioxidants. Generally, antioxidant effectiveness is assessed by comparing their relative improving effect on oxidation stability, which can be characterised using oxidation stability test methods that are described later in this review.

1.3.1. Tocopherols

Tocopherols are well understood antioxidants (more commonly known as vitamin E) and occur naturally at varying levels in plant oils, dependent on the oil refining process, which may or may not remove them. Even after refining, 500–1000 ppm can still be present, though distillation will remove any tocopherols originally present [13]. Tocopherols present in the parent vegetable oil can also be present in biodiesel, depending on the production process used; some biodiesel production processes include a distillation step for purification of the methyl esters. Biodiesel made from rapeseed oil tends to be very stable in terms of oxidation, due to high tocopherol content of the pure oil. Soy oils, for example, were reported [9] to contain between approximately 500 to 3000 ppm of tocopherols along with other antioxidants, such as sterols and tocotrienols, with levels unaffected by the FAME preparation process.

Tocopherols are phenolic antioxidants that occur in four isomers: alpha, beta, gamma and delta. They all have the same basic chemical structure: a hindered aromatic phenol structure is bonded to a long-chain phythyl group. Each fatty oil has a unique amount and distribution of these four tocopherols. The gamma and delta isomers appear to be the most effective in fatty oils. Tocopherols are only present at trace levels in animal-derived fats. Studies indicate that naturally occurring levels of tocopherols in vegetable oils are close to optimal, and intentional use of additional amounts can provide no further benefit and sometimes decreases stability. However, tocopherols are much less effective than synthetic antioxidants when added to fatty oils and esters [13].

1.3.2. Synthetic antioxidants

Some of the more effective synthetic antioxidants include: tertiary butylhydroquinone (TBHQ), pyrogallol (PY) and propyl gallate (PG). Effective concentrations are usually between 200–1000 ppm, depending on substrate and the type of stability test used to evaluate additive performance. 2,6-di-*t*-butyl-4-methylphenol (BHT) is one of the most effective synthetic antioxidants in hydrocarbon fuels and lubricants, though is usually one of the least effective in fatty oils and esters [13]. In the same way, tocopherol is generally effective in hydrocarbon fuels and lubricants despite relatively poor performance in fatty oils and esters. Little work has been done on other antioxidant types, which may have potential though many can have adverse effects, decreasing stability. Natural tocopherol antioxidants exhibit poor performance when compared to synthetic antioxidant additives. Using various stability test methods for methyl esters, study results have consistently shown common synthetic antioxidants to be superior to tocopherols [13]. In some studies tocopherols have even been shown to decrease methyl ester stability. One such synthetic antioxidant that has been shown to exhibit superior performance among other synthetic antioxidants is *t*-butyl hydroquinone (TBHQ)[1], which is frequently found to be the best overall performer in biodiesel methyl esters [13]. Baynox® is an example of a commercially available synthetic antioxidant for biodiesel application, being a chemical simulation of alpha-tocopherol (vitamin E) [12].

2. Techniques for oxidation stability characterization

Oxidation stability of biodiesel can be characterized by a number of different metrics; each providing information on a certain aspect of fuel stability. A multitude of test procedures have been developed. Some measurements indicate the propensity of material to oxidize, whilst others indicate levels of oxidation products. More elaborate tests involve acceleration of fuel sample oxidation usually by controlled oxygen exposure at elevated temperatures, over a measured time—oxidation product levels are monitored, so that the relative resistance to oxidation of a fuel can be assessed. For example, quantities of filterable insoluble materials may be measured in such tests, or acid levels may be continuously monitored; giving rate information on the progression of oxidation.

Techniques for characterization of oxidation stability can be categorized according to what is measured: initial fatty oil composition, primary oxidation products, secondary oxidation products, physical properties, or some other parameter indicative of relative stability. Measurements that can be made to characterize the oxidation stability of biodiesel include those (non-exhaustively) listed below:

- Compositional analysis
  - Gas or liquid chromatography methods
  - Various structural indices based on composition, such as: Iodine Value (IV), APE, BAPE, OX.
  - FFA, free and total glycerol content
  - Electromagnetic spectroscopy
- Primary oxidation product levels
  - Peroxide Value (PV)
- Secondary oxidation product levels
  - Anisidine Value (AnV) (aldehyde content)
  - Total Acid Number (TAN)
  - Polymer levels
  - Quantities of filterable insoluble materials present
- Physical properties
  - Viscosity and density
- Accelerated oxidation tests, such as:
  - Oil Stability Index (OSI) or Rancimat induction period (RIP)
  - Pressurized-differential scanning calorimetry (P-DSC)

Some measurements are less suitable for monitoring oxidation progression. For example, PV is less suitable as it tends to increase initially as peroxides form and then decrease upon further oxidation, as peroxides react to form secondary products [18]. No one measurable parameter or stability test appears to be adequate to define all the stability characteristics of biodiesel fuel. It is unlikely that any one new test will be able to completely define biodiesel stability [13]. Consequently, several measurements are required in order to adequately characterize stability.

2.1. Fuel quality parameters related to oxidation stability

Table 1 details fuel properties, test methods and limit values adopted by respective European (EN 14214) and United States (ASTM 6751) biodiesel fuel quality standards. Additionally, the European standard EN 14213 defines the minimal requirements for biodiesel to be used as heating oil or as a blending component for heating oil.

ASTM D 6751 [25] and EN 14214 [26] specify several parameters that are related to oxidation stability, and these are listed in Table 1. Specifications on iodine value, linolenic acid content and content of FAME with ≥ 4 double bonds each serve to limit the relative susceptibility of material to oxidization. Oxidation stability is directly characterized according to the standard test method EN 14112, which is an accelerated oxidation test that directly measures oxidation propensity; known as the Rancimat method. Levels of trace metals also strongly influence oxidation stability, as discussed further in Section 3.2.1.

Ester content, total contamination, acid number, kinematic viscosity, and density are all affected by the formation of oxidation products, so that changes in these properties can indicate the progress of oxidative degradation. Heating value, flashpoint and Cetane number are also affected, for example by the formation of hydroperoxides. Other EN 14214 parameters that may be influenced by oxidative degradation include: water content, copper-strip corrosion and carbon residue [1]. Biodiesel fuel quality can deteriorate and fall out of spec relatively rapidly as the fuel ages during storage. For example, Bondioli et al. [27] presented data showing biodiesel fuel stored at 43 °C falling out of spec on acid number, viscosity, ester content and other properties over a 24 week period. Bondioli et al. [27] remarked at the lack of knowledge with respect to evaluation of oxidation, storage and thermal stability of biodiesel at the time of the EN 14214 standard's inception, and noted the preliminary and evolving nature of specifications that “might be improved in the future when further knowledge should be available”.

Table 1
Comparison of EU and US biodiesel specifications.

BIODIESEL PROPERTY	EN 14214/213	EN 14214	EN 14213	ASTM D 6751		Comments comparing EU vs. US spec
	Test method	Limits		Test method	Limits	
Oxidation stability [h]	EN 14112	> 6	> 4	EN 14112	> 3	*US spec more lenient*
Iodine value [(g) I_2/100 g]	EN 14111	< 120	< 130	–	–	*No IV spec for US*
Acid number (acid value) [mg KOH/g]	EN 14104	< 0.5		ASTM D 664	< 0.5	*Similar*
Water content [mg/kg]	EN ISO 12937	< 500		ASTM D 2709	< 500	*Similar*
Group I alkali metals (Na+K) [mg/kg]	EN 14108 EN14109	< 5.0	–	EN 14538	< 5.0	*Similar*
Group II Earth metals (Ca+Mg) [mg/kg]	EN 14538	< 5.0	–	EN 14538	< 5.0	*Same*
Total glycerin [% mass]	EN 14105	< 0.25	–	ASTM D 6584	< 0.24	*Similar*
Distillation temperature [°C]	–	–	–	D1160	< 360	*No EU spec on distillation temp*
Methanol content [% m/m]	EN 14110	< 0.20	–	–	–	*No US spec on methanol content*
Copper strip corrosion (3 h, 50 °C) [rating]	EN ISO 2160	Class 1	–	D 130	No. 3 Max	*Both EU and US specify corrosion rating*
Phosphorous content [mg/kg]	EN 14107	< 10.0		D4951	< 10	*Similar*
Ester content [% (m/m)]	EN14103	> 96.5		–	–	*No US spec on ester content*
Density @15 °C [kg/m^3]	EN ISO 3675 ENISO 12185	860––900		–	–	*No US spec on density*
Viscosity @ 40 °C [mm^2/s]	EN ISO 3104 ISO3105	3.5–5.0		D 445	1.9–6.0	*Similar, US slightly more lenient*
Flash point [°C]	EN ISO 3679	> 120		D 93 (closed cup)	> 130.0	*US slightly more conservative on flashpoint*
Sulfur content [mg/kg]	EN ISO 20846 ENISO 20884	< 10.0		D 5453	< 15 or < 500	*US more lenient on sulfur. For S15 and S500 grades of biodiesel, respectively.*
Carbon residue [or Tar remnant] (10% dist. residue) [% m/m]	EN ISO 10370	< 0.30		D 4530 (100% sample)	< 0.05	*Both EU and US specify carbon residue limit*
Sulfated Ash [% m/m]	ISO 3987	< 0.02		D 874	< 0.02	*Similar*
Total contamination [mg/kg]	EN 12662	< 24		–	–	*No US spec on insoluble contaminants*
Content of FAME with ≥ 4 double bonds [% m/m]	EN 14103	< 1		–	–	*No US spec on ≥ 4 double bonds*
Linolenic acid content [% m/m]	EN 14103	< 12	–	–	–	*No US spec on linolenic content*
Mono-glyceride content [% m/m]	EN14105	< 0.80		–	–	*No US spec on residual glycerides*
Di-glyceride content [% m/m]	EN14105	< 0.20		–	–	"
Tri-glyceride content [% m/m]	EN14105	< 0.20		–	–	"
Free glycerine [% m/m]	EN14105 EN14106	< 0.02		D 6584	< 0.02	*Similar*
Cold filter plugging point [°C]	EN 116	–	–	–	–	*No US spec on CFPP*
Cloud point	–	–	–	D2500	report	*No EU spec on cloud point*
Pour point [°C]	ISO 3016	–	< 0	–	–	*Pour point spec only for heating oil*
Heating value [MJ/kg]	DIN 51900-1	–	> 35	–	–	*Heating value spec only for heating oil*
Cetane Number	EN ISO 5165	> 51	–	D613	≥ 47	*US more lenient on cetane number*

2.1.1. Iodine value

The "iodine value (IV)" or "iodine number" is a stability index measuring levels of unsaturation in organic compounds, such as FAME. The IV is defined as the mass of iodine (grams) that can be formally added to 100 g of the sample, measured according to the standard test method EN 14111. It is an indicator of the number of double bonds present in the sample; the higher the IV, the higher the number of double bonds [12]. The IV of a particular TAG is almost identical to that of the corresponding methyl esters, although IV decreases with higher alcohols used in transesterification [18]. Iodine Value is one of the oldest and most common methods for determining the level of unsaturation in a fatty oil or ester [13]. Iodine Value of a pure compound can be theoretically calculated by Eq. (11).

$$\mathrm{IV_{pure}} = 100 \times \frac{253.81 \times db}{\mathrm{MW}_f} \tag{11}$$

where db=number of double bonds, MW_f=Molecular Weight of the fatty compound, and 253.81 is the atomic weight of the two iodine atoms that are theoretically added to one double bond [28]. Accordingly, the IV of a mixture of fatty compounds can be calculated by Eq. (12).

$$\mathrm{IV_{mixture}} = \sum A_f \times \mathrm{IV_{pure}} \tag{12}$$

where A_f=the amount (%wt) of a particular fatty compound in a mixture.

Eqs. (11) and (12) assume full iodination. It can be seen that IV depends on the MW of the component unsaturated compounds. The idea behind the use of IV is that it would indicate the propensity of an oil or fat to oxidize, and so may indicate the tendency of biodiesel to polymerize and form engine deposits. Hence an IV maximum of 120 is specified by EN 14214.

However, IV does not depend on the exact nature of the double bonds in the structure; it establishes only the relative concentration of unsaturation within a sample. It provides no information on the distribution of double bonds in an ester chain molecule so that the number of allylic and bis-allylic sites remains unknown. Iodine Value treats all double bonds as being equally reactive, therefore cannot be a predictor of oxidation stability [5]. It has been shown that different fatty acid structures can give the same IV [12]. Two samples with the same IV can therefore exhibit entirely different oxidization behaviour. Knothe and Dunn [5] discussed these inadequacies and showed that IV is insufficiently precise to justify its inclusion in biodiesel fuel quality standards. Knothe [28] pointed out also that the IV specification of EN 14214 unnecessarily excludes several important feedstock vegetable oils including soybean and sunflower. In fact, IV has been shown to not correlate with other measurements of oxidation stability [5,13], and IV tends to decrease with ageing [3] so that a more oxidized sample has a lower IV. Consequently IV is understood as a rough indicator of stability. Other indices such as APE and BAPE as well as the Rancimat test, discussed below, serve to characterize FAME susceptibility to oxidation more accurately [12].

2.1.2. Linolenic acid and ester content

The content of methyl linolenate is restricted in EN 14214 because of its high propensity to oxidize. However, the 12% limit is set so as not to exclude high oleic rapeseed oil; one of the major European biodiesel feedstocks [29]. FAME or ester content diminishes as esters degrade by oxidation, so that this measurement can serve to indicate oxidation progress. For example, Lacoste and Lagardere [30] presented data showing deterioration in FAME content, and other parameters with oxidation. Both linolenic acid and ester content can be determined by Gas Chromatography according to standard test method EN 14103.

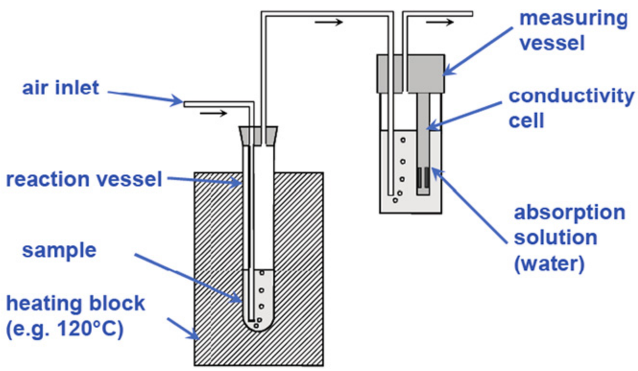


Fig. 1. Principle of the Rancimat method.

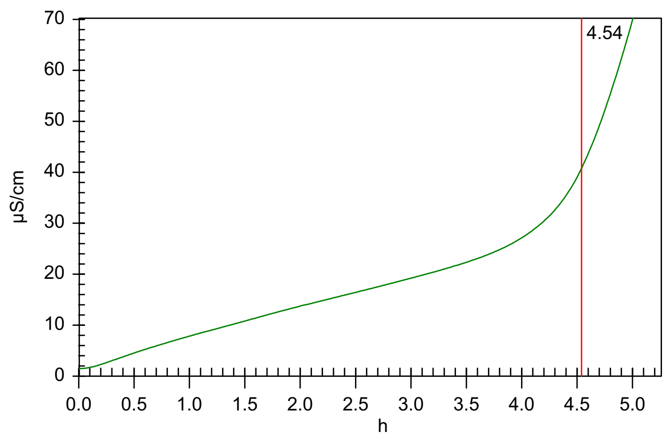


Fig. 2. Example Rancimat test data: conductivity (μs/cm) vs. test duration (h) for a rapeseed biodiesel sample, RIP = 4.54 h.

2.1.3. Content of FAME with ≥4 double bonds

This specification serves to eliminate fish oils as biodiesel feedstock. With their even higher content of methylene interrupted double bonds, fish oil fatty acids are even more susceptible to oxidation than linolenic acid and its esters, with 3 double bonds [29].

2.1.4. Oxidation stability by the Rancimat method

The susceptibility of biodiesel to oxidation due to unsaturated ester content prompted establishment of the standard test method EN 14112, for the characterization of biodiesel oxidation stability. The Rancimat method utilizes an instrument such as the 873 Biodiesel Rancimat, manufactured by Metrohm. The Rancimat method is nearly identical to the Oil Stability Index (OSI) method, which is an AOCS (American Oil Chemists' Society) method [7,18]. The terms "Rancimat" and "OSI" are often used interchangeably in the open literature, when referring to this type of test method.

The automated EN 14112 test as shown in Fig. 1 involves passing air at a steady rate (10 l/h), through a 3 g sample held in a reaction vessel which is heated to a specified temperature (110 °C). The air passes out of the sample carrying volatile, water-soluble short chain carboxylic acids (secondary oxidation products) into a measuring vessel containing an absorption solution of distilled water, in which conductivity is continually monitored by cell electrodes. A rise in cell conductivity indicates accumulation of volatile acids in the water, due to oxidation of the sample. The primary volatile acidic species is formic acid. A chemical mechanism to explain the decomposition of hydroperoxides to formic acid has been proposed [13].

Oxidation of the sample proceeds slowly at first so that the increase in conductivity initially measured is small. Oxidation gradually accelerates with a steady climb in conductivity readings, resembling an exponential growth curve. The curve gradient

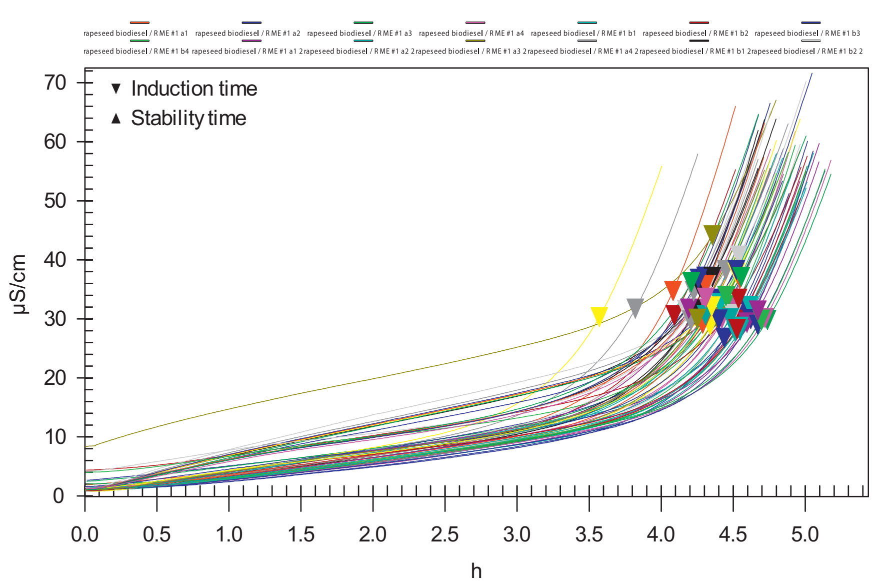


Fig. 3. Rancimat test-cell conductivity (μs/cm) with time (h), displaying 64 replicate oxidation stability determinations for the same Rapeseed Methyl Ester (RME).

increases to a maximum value and then decreases. The "induction period" (IP) is evaluated by the automated Rancimat software, which calculates the maximum second derivative of conductivity with respect to time [12]. The induction period is determined as the duration (h) of the test up until this maximum point as shown in Fig. 2. Recently, the present author investigated the reproducibility of oxidation stability measurements made by the Rancimat method. Fig. 3 shows determination (conductivity curve) results for 64 replicate tests. The maximum second-derivative (point of maximum acceleration) of each conductivity curve is defined as the Racimat Induction Period (RIP), or Induction time (h). Fig. 4 shows a histogram of induction time results for the grouped RIP data (group intervals were $X-0.05$ to $X+0.049$). Repeatability of measurements was generally good, with the exception of 2 low outliers. The histogram shows a near normal distribution with the exception of the low outliers. Statistical analysis of measurements indicated a 99% confidence of a measurement lying within $+/-0.6$ of the mean (4.40 h).

The Rancimat method characterizes the oxidation stability of biodiesel (as well as fats and oils) by accelerating the oxidation process; heating to a fixed temperature, far above ambient and exposing the sample to a controlled flow of air. The Rancimat method has become an integral element of standards for biodiesel fuels and their blends [12]; in EN 14214 and ASTM 6751. Under EN 14214 specifications, biodiesel fuels are required to meet an IP of at least 6 h when tested at 110 °C with a constant air flow of 10 l/h, according to EN 14112 [18]. This limit is anticipated to increase to 8 h [31]. It is well known that it is very difficult to meet this limit for biodiesel fuels derived from many common feedstocks, unless antioxidants are added to the biodiesel [32]. In comparison, it should be noted that ultra-low sulfur diesel is very stable with an IP of over 36 h [8].

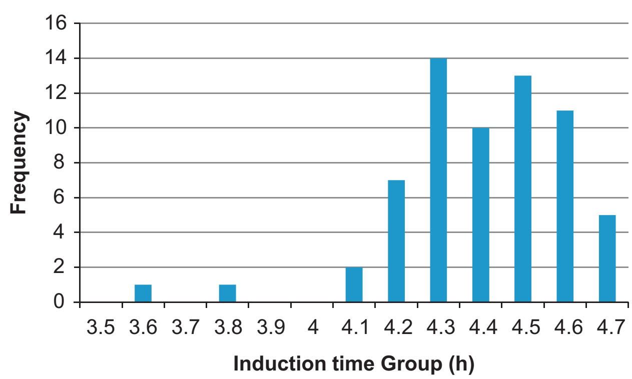


Fig. 4. Histogram of induction times for 64 replicate determinations.

A survey of fuel quality carried out across 24 retail stations in the US by Tang et al. [8] found overall quality to be acceptable except for the oxidation stability – determined according to EN 14112 – where over 45% of samples failed to achieve an IP of 6 h or longer. In another study, Ramos et al. [32] determined oxidation stability according to EN 14112, for a range of biodiesels derived from: olive, rape, soybean, sunflower, grape, high oleic, sunflower, almond and corn oils. All the biodiesels failed to achieve the minimum 6 h limit. Antioxidant treatment is a straight forward method to increase resistance to oxidation.

Several studies have shown that if Rancimat IP measurements are repeated at various test temperatures between 50 and 220 °C, and other test parameters (FAME sample, mass, air flow rate etc.) are held constant, then the logarithm of IP emerges as a linear function of test temperature (T), so that log(IP) plotted vs. T gives a straight line [13]. The authors Xin et al. [33] presented data demonstrating this dependence for safflower biodiesel, dosed with various concentrations of synthetic antioxidant. This relation is consistent with the Arrhenius equation that describes increased reaction rate at higher temperature, according to which a temperature reduction of 10 °C should result in an approximate doubling of the induction time. Thus it is possible for RIP determination results to be extrapolated in order to predict stability at the prevailing ambient temperature [12]. Rancimat test data (collected by the present author) for Rapeseed oil samples demonstrates this relationship as shown in Fig. 5.

The author Dunn [1] investigated the effects of temperature on the OSI of biodiesel, demonstrating Arrhenius temperature dependence and extrapolation of result temperature curves; details of this work are reviewed in Section 3.2.4. The strongly temperature dependent nature of oxidation behaviour is evident, along with the observation that lower biodiesel storage temperatures should significantly delay the onset of oxidation. A line of best fit applied to test data shown in Fig. 5, shows the induction period corresponding to a test temperature of 20 °C can be read to be ~4000 h (167 day, around 6 months); implying the Rapeseed oil from which the sample was taken, might endure storage at 20 °C for around 6 months prior to the onset of rapid oxidation. At 10 °C storage temperature it is

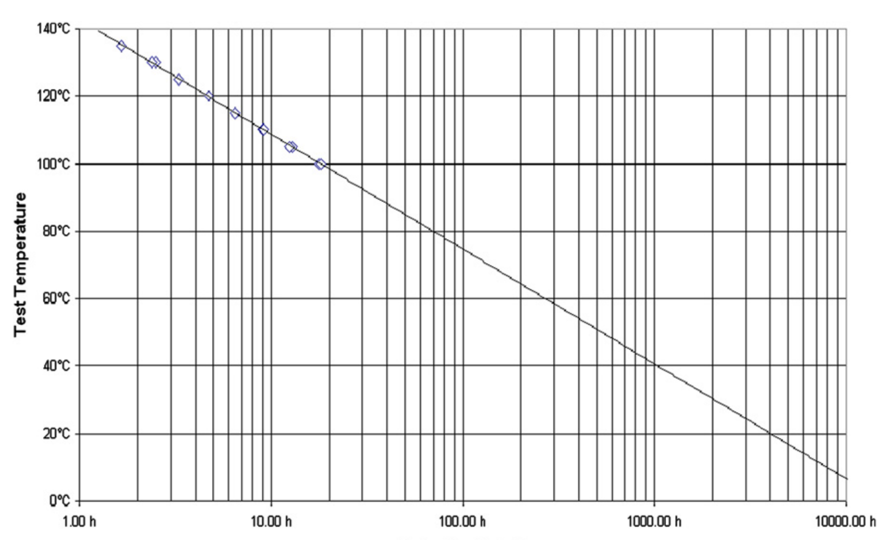


Fig. 5. Test temperature vs. log (RIP): extrapolated data for fresh, refined Rapeseed oil.

implied the oil may endure around twice as long; suggesting cold storage of biodiesel as a method for delaying oxidation. Xin et al. [33] similarly extrapolated RIP data for safflower biodiesel dosed with various concentrations (0–5000 ppm) of synthetic antioxidant, (propyl gallate) to obtain estimates of the induction period at 25 °C. These estimates showed dramatic improvement in storage life made possible by antioxidant dosing, though improvements gradually diminished as dose increased, reaching a plateau.

However, storage life estimates based on RIP measurements may be unreliable since it is assumed the oxidation mechanism does not alter at the extrapolated lower temperatures. Bondioli et al. [34] commented to this effect, noting that attempting to speed up the oxidation processes happening at ambient temperature by simply increasing reaction temperature can only give a measure of the sample reactivity. Factors such as activation energies and gas solubility are affected by altering reaction temperature, so that samples aged by an accelerated test will have dramatically different properties to that of the same samples after a long period of natural ageing at ambient temperature. Likewise, Dunn [35] showed extrapolation of the Arrhenius curve down to low temperatures becomes unreliable (see Section 3.4). In this context, a limitation of the Rancimat accelerated test method is apparent: it is not a substitute for actual storage tests in terms of understanding how biodiesel properties change under different real-world storage conditions. However, the accuracy and utility of storage life estimates is in need of further investigation.

A further limitation of the Rancimat test (EN 14112) is that it lacks the ability to characterize the tendency of biodiesel oxidation that results in the accumulation of insoluble materials; a potential cause of engine problems as discussed earlier. The Rancimat test is more suited to demonstrating how long biodiesel can withstand oxidative conditions, rather than its inherent tendency to form polymers. Although studies have shown, there is general correlation where samples with long induction times (> 2 h) exhibited lower levels of insolubles [9]. The correlation of such measurements also warrants further investigation.

While EN 14112 is valid for testing only pure biodiesel fuel samples, modified method EN 15751 enlarges applicability of the test to blends of biodiesel (> 2%v/v) with petro-diesel [21]. This method, which is otherwise the same as EN14112, specifies a larger sample mass (7.5 g), longer reaction vessels (increased from 150 to 250 mm in length) and a slightly greater volume of absorption solution (60 ml distilled water). The evaluation of RIP is also performed manually (and not automatically by the software) [31]. These changes are mainly due to higher volatility of hydrocarbon fuels compared to methyl esters, which may lead to higher sample evaporation. Biodiesel blends with petro-diesel are required to obtain a minimum RIP of 20 h at 110 °C to comply with European fuel quality standards [31].

2.1.5. Total contamination

Standard test method EN 12662 is a filtration method for determination of insoluble contaminant levels. The test involves a weighed biodiesel sample filtered under vacuum through a pre-weighed filter of specified porosity. The contaminated filter with insoluble residue is washed, dried and weighed. Contamination deposited on the filter is then calculated relative to the sample mass [mg contamination/kg sample].

2.1.6. Acid number

Acid number (AN), Acid value (AV), or Total acid number (TAN), indicates the quantity of fatty acids and mineral acids (negligible) present in a biodiesel sample. As discussed earlier, high fuel acidity is associated with corrosion and engine deposits, particularly in the fuel injectors. AN can be determined by titration according to test method EN 14104, using a dilute ethanolic KOH solution [29]. A test sample is dissolved in solvent, and diluted KOH solution added, using a pH indicator to detect the end point. AN is expressed in mg KOH required to neutralize 1.0 g of the biodiesel sample [12]. Acid number is useful in monitoring degradation of biodiesel during storage since AN increases with degradation. Esters first oxidize to form peroxides which then undergo complex reactions, including a split into more reactive aldehydes which further oxidize into acids [3]. Monitoring AN can indicate ongoing fuel degradation—by oxidation, or by hydrolysis of esters into alcohol and FFAs due to the intrusion of water [3].

Acid number has an important role in quality control of both TAG feedstocks for biodiesel, as well as finished biodiesel. Generally, feedstock TAG should have AN below 1.0 mg KOH/g [12]. Higher feedstock AN reduces the base-catalyzed transesterification ester yield; catalyst is consumed (neutralized) forming contaminant soaps. Feedstocks with high ANs should preferably be processed to biodiesel via an acid catalysed esterification, where FFAs are converted to methyl-esters. The acid-catalysed reaction can be carried out as a prior stage to base-catalysed transesterification.

2.1.7. Viscosity

Formation of polymeric secondary oxidation products increases viscosity and can lead to the formation of gums and sediments that clog filters. Viscosity is thus a useful measure for monitoring oxidation progression. Kinematic viscosity is most often measured and can be determined according to standard method EN ISO 3104, using a temperature controlled bath and a suitable calibrated glass capillary viscometer. The time for a volume of liquid to flow under gravity through the viscometer is measured, and converted to a viscosity reading.

The kinematic viscosity range prescribed in EN 14214 serves to exclude vegetable oils as fuel, in preference to their FAME derivatives as well as restrict the fatty acid profile, by excluding shorter-chain fatty acids. The acceptable range of kinematic viscosity prescribed in EN 14214 is slightly higher than that acceptable for petrodiesel fuels—EN590 limits are 2.0–4.5 mm^2/s according to EN ISO 3104. Biodiesel fuels derived from used frying oils tend to possess higher viscosity than those from most vegetable oils, owing to their higher content of *trans* FA and more saturated FA, therefore the upper EN 14214 limit of 5.0 mm^2/s may exclude some of these oils [29].

2.1.8. Density

Density is determined according to EN ISO 3675 by hydrometer reading, at a set temperature. Hydrometers with a specific range are required for measurements of biodiesel density at different temperatures, using a temperature controlled bath. The purpose of the density specification in EN 14214 is to exclude extraneous material as biodiesel feedstock [29].

2.2. Further measurements

Other parameters beyond those specified by EN 14214 (discussed below) can improve the characterization of biodiesel oxidation stability. More detailed examination of FAME composition, oxidation products and physical properties is possible, as are several alternative (to Rancimat) accelerated oxidation tests.

2.2.1. Compositional analysis

In order to better characterize biodiesel propensity to oxidize, a complete knowledge of fatty acid composition is desirable; establishing the relative proportions of oleic, linoleic, linolenic and other fatty acids. Standard test method EN 14103 is Gas

Chromatography procedure which enables the determination of FAME composition; results provide information on the degree of fatty acid chain unsaturation of component FAMEs, allowing the determination of stability indices described below.

Allylic Position Equivalent (APE) and bis-allylic Position Equivalent (BAPE) are special indices developed to consider the amount of allylic or bis-allylic carbons, which appear more suitable for assessing oxidative stability than IV [5]. BAPE and APE indices can be determined by chromatographic or spectroscopic methods such as GC or NMR [28]. The BAPE value is more significant for oxidation of unsaturated fatty compounds due to the significantly higher relative rate of oxidation of bis-allylic CH_2 positions [5]. Linoleic acid has one bis-allylic site and two allylic sites. Linolenic acid has two bis-allylic sites and two allylic sites. Oleic acid has one double bond at Δ9, meaning two allylic sites; one at C-8 and the other at C-11.

Oleic acid: $HOOC–(CH_2)_7–CH{=}CH–(CH_2)_7–CH_3$

Autoxidation proceeds at different rates depending on the number and position of double bonds. Allylic sites are especially susceptible to oxidation and bis-allylic sites even more so. Knothe [28] presented methods for the calculation of APE and BAPE indices, outlined below. One APE is the equivalent of one allylic site contained in a fatty compound of concentration 1% in a mixture. The common fatty compounds: C18:1, C18:2 and C18:3 each contain two allylic sites, so that Eq. (13) holds:

$$APE = 2 \times (A_{C18:1} + A_{C18:2} + A_{C18:3}) \tag{13}$$

where A = %wt. of respective C18 compounds. More generally this is written as Eq. (14):

$$APE = ap_a \times A_{Ca} + ap_b \times A_{Cb} + ap_c \times A_{Cc} + \cdots \tag{14}$$

where ap_x = is the number of allylic sites in specific fatty acids (FA), and A = %wt amount of each FA in a mixture.

One BAPE is the equivalent of one bis-allylic site contained in a fatty compound of concentration 1% in a mixture. C18:2 contains one bis-allylic site, C18:3 contains two, giving Eq. (15):

$$BAPE = (A_{C18:2} + 2 \times A_{C18:3}) \tag{15}$$

The APE and BAPE indices can be divided by the factor 100 to yield the average number of allylic or bis-allylic positions per molecule, in a mixture of fatty compounds. BAPE value is the more significant for oxidation of unsaturated fatty compounds due to the significantly higher relative rate of oxidation of bis-allylic CH_2 positions [5].

For fatty compounds with conjugated double bonds, or with two double bonds separated by more than one CH_2, then BAPE = 0. The two indices can only be correctly calculated from FAME analysis results of fatty oils and esters that contain methylene-interrupted structures, such as rapeseed or soy. For oils that do not have methylene-interrupted poly-olefinic unsaturation structure, such as jojoba oil and meadow foam oil, the APE and BAPE formulae are not valid [36].

The limited structural information (inadequacy) of IV can be demonstrated by considering the minimum and maximum BAPE values possible for a sample of constant IV. Knothe and Dunn [5] showed that for a constant IV = 115, $BAPE_{min}$ = 33.87 (for hypothetical oil of only C18:1 and C18:2), whilst $BAPE_{max}$ = 88.32 (for hypothetical oil of only C18:3 and saturated compounds). Knothe and Dunn [5] evaluated BAPE values for mixtures of methyl esters (C18:0, C18:1, C18:2, C18:3) in various controlled proportions. A linear correlation with OSI times was reported, with OSI times decreasing as BAPE values increased. However, the authors concede that this approach did not consider the contribution to oxidation of the allylic positions, hence further research appears necessary to quantify the contribution of the allylic positions, relative to the more oxidation-prone bis-allylic positions [5].

Oxidizability (OX) is another stability index calculated according to Eq. (16) from knowledge of the oleic (O), linoleic (L) and linolenic (Ln) acid compositions (%wt). Equation coefficients are derived from kinetic studies and are proportional to the relative rates of oxidation of these compounds [9]. For oils with methylene-interrupted unsaturation, the formula is similar to APE and BAPE as it recognizes the importance of allylic and bis-allylic carbons [13]. The OX parameter applies only to biodiesel or fat containing predominantly 18 carbon fatty acid chains [9].

$$OX = [0.02(\%O) + (\%L) + 2(\%Ln)]/100 \tag{16}$$

Measurement of antioxidant content can also serve as an index. Several methods to directly measure tocopherols or to indirectly measure the impact of natural antioxidants have been proposed. High performance liquid chromatography (HPLC) methods have been developed to measure tocopherols. ISO 9936 is a HPLC method used in the biodiesel industry [13]. Other methods exist as discussed by Waynick [13] that measure "antioxidant power"; involving measurements by electrical potential, or by detection of colour spectra.

Meira et al. [37] recently developed a new, alternative analytical methodology for the determination of oxidation stability, which was shown to reliably predict oxidation stability of oils and biodiesel. Predictions of oxidation stability obtained by the new methodology showed good agreement with results obtained by the Rancimat method (EN 14112). The analytical technique used a combination of spectrofluorimetry and multivariate calibration, where measurements were performed on a Perkin Elmer spectrofluorometer. Spectrofluorimetry is a non-destructive analytical technique, which allows the reliable, direct and fast determination of several properties, without sample pre-treatment. It involves application of ultraviolet light which excites electrons of molecules causing them to emit radiation of specific wavelength, which allows compositional characterisation from the emitted spectra. It is widely used in chemical analysis due to its high sensitivity and specificity [37].

Advantages of the technique for application to biodiesel oxidation stability measurement include a much shorter analysis time, and the potential for on-line monitoring. For example, the study authors [37] reported that oxidation stability could be determined by the new technique in approximately 20 min, including analysis time. Fast, accurate analysis would overcome the main disadvantages of the current Rancimat method, which is time consuming and also suffers problems with reproducibility, as discussed in a separate study by Karavakalis et al. [31] (see Section 3.7).

2.2.2. *Primary oxidation products—Peroxide value*

Peroxide value (PV), measured in milliequivalents of peroxide per kg of sample indicates the content of primary products of oxidation; hydroperoxides. Thus low PV is favourable for high oxidation stability in biodiesel [3]. Hydroperoxides can be measured by standard method ASTM D3703. Conjugated dienes that are also primary products from methylene-interrupted isomers can be measured by UV adsorption as per ISO 3656 [13].

As mentioned earlier, PV is a less suitable indicator of oxidation progression because peroxides readily decompose (especially in the presence of contaminating catalysts), thus PV tends to increase to a maximum and then decrease as secondary products are formed [5]. Although PV is not specified in biodiesel fuel standards, this parameter influences the cetane number (CN) which is specified in fuel standards; increasing PV increases CN [3].

2.2.3. *Secondary oxidation products*

Secondary oxidation products: aldehydes, alcohols, short chain carboxylic acids, and higher molecular weight oligomers, can be

measured by various procedures. Acid Number (see above), Anisidine Value and chromatography methods for polymers are among the most important.

Anisidine value (AV or AnV) indicates the levels of aldehydes in oxidized fatty oils and esters (EN ISO 6885).

Polymer levels can be measured by a standard procedure often used in the biodiesel industry; BS EN ISO 16931, which uses HPLC with a refractive index detector (polymers have higher refractive indices) [13].

TOTOX is an index that has been proposed, designed to track the oxidation process and account for both primary and secondary oxidation products. It is based on a weighted linear sum of peroxide value and anisidine value [13], according to Eq. (17):

$$\mathrm{TOTOX} = 2 \times \mathrm{PV} + \mathrm{AnV} \quad (17)$$

ASTM D2274 is a standard test method for determining insoluble formation, developed for petroleum products. Oxidation of a sample is accelerated by heating to 95 °C and exposure to oxygen bubbling for 16 h. The sum of sediment (filterable insolubles) and gum (adherent insolubles) is reported in mg/100 ml of sample, using filtration and weight measurements to infer the quantities of insolubles produced. The propensity of the material tested to form deposits (oligomers and or polymers) under highly oxidizing conditions is thus measured [9]. *ASTM D4625* is another method of this type; measuring insolubles by filtration as an indication of fuel instability.

2.2.4. Physical properties

Other physical properties that can characterize fatty oil oxidation include refactive index (see polymer levels above), and dielectric constant, which may be used to measure levels of oxidation products more polar than the original substrate.

2.2.5. Accelerated oxidation tests

In addition to the Rancimat method described above, other accelerated oxidation test procedures exist. The Schaal oven test is one of the oldest methods, where a convection oven is held at a specified temperature containing open fatty oil samples. The endpoint of the test is determined by measurement of chemical parameters, such as observing a rapid increase in PV, or by observing rapid weight gain of a sample due to incorporation of oxygen in to the oil.

The oxygen adsorption (uptake) test is where a sample is heated in a closed vessel while measuring oxygen content of the headspace. A sudden rise in the rate of oxygen consumption indicates the onset of rapid oxidation.

Active Oxygen Method (AOM) (AOCS Cd 12-57): has been used for decades in various guises—it involves heating a sample to a set temperature while bubbling dry air through at a steady rate. The endpoint is when a threshold PV value is achieved and the time taken for this is to occur is measured. Or the endpoint can be taken to be when a rapid increase in PV is observed.

Pressurized differential Scanning calorimetry (PDSC): has been used in several oxidation stability studies of fatty oils and esters. When run using an isothermal procedure, the time required to detect an exothermic reaction is considered the induction time. When run using a non-isothermal procedure, the temperature where an exothermic peak is detected is called the oxidation temperature (OT) [13].

Jain and Sharma [36] also reviewed and compared different test methods for characterization of biodiesel instability and concluded the most useful and beneficial method was the EN 14112 Rancimat test method, as well as ASTM 2274; in terms of the ability of the test to discriminate between biodiesel samples of various levels of oxidation stability, ease of use, and ability to discern additive effects.

2.3. Correlation of stability measurements

Correlations between biodiesel oxidation stability measurements have been examined by several authors [9,13,30]. Rancimat/OSI data correlate well with other stability test results, including PV, AN, ASTM D525 and PDSC test results [13]. Lacoste and Lagardere [30] showed that Rancimat IP is well correlated to degradation in other quality parameters, including: PV, polymer content, AV, AnV, viscosity, and ester content.

AN and viscosity correlate well; indicating polymeric material – the cause of higher viscosity – is formed in a way related to acidic compound formation. Oxygen availability is noted to be of crucial importance to behaviour in test properties; when oxygen is limiting then secondary product formation (acids, polymers) are slowed [13].

However, the amount of total insolubles that are formed in biodiesel oxidation, do not appear to correlate with IP, or any other parameters that correlate with IP. There is said to be "a major disconnect between common stability parameters and the amount of insolubles formed" [13]. Antioxidant levels, sample storage/handling conditions and test procedure variables are some factors cited [13] that can influence insoluble levels reported. Glycerine content appears to be another important factor contributing to this disconnect.

McCormick et al. [9] examined insolubles formation by the ASTM D2274 method; testing 27 different commercially available U.S. biodiesels. Results for total insolubles did not correlate well with Rancimat IP although a general trend was evident in that samples with a longer IP (> 2 h) exhibited relatively low levels of insolubles as shown in Fig. 6. Non-correlation was attributed by the authors to differences in the test methods. However details of specific differences to blame were not discussed. It is evident that one major difference is the duration of respective tests, which can differ widely—the test for insolubles involves heating a sample to 95 °C and exposure to oxygen for 16 h. Whereas Rancimat test durations at 110 °C are typically much shorter. Rancimat IP and

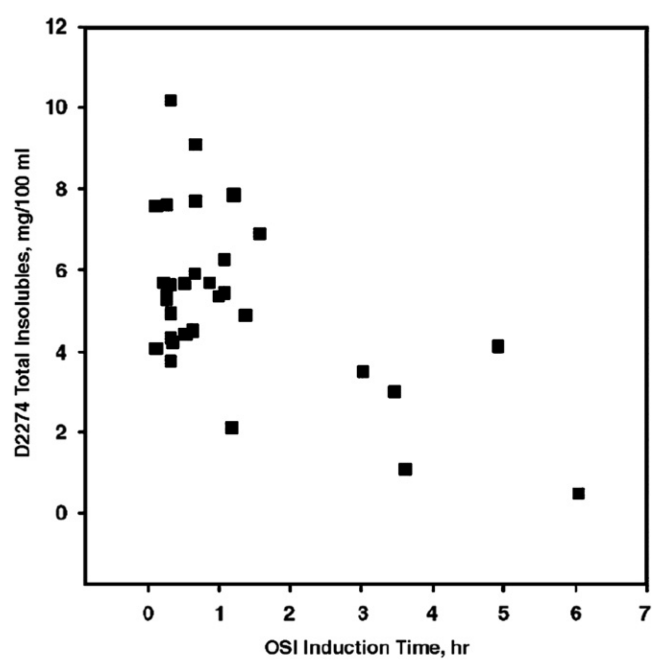


Fig. 6. Comparison of stability test data: total insolubles vs. OSI times [9].

insolubles data might correlate better if test conditions (temperature and duration) were better harmonized. It appears further study in this area is warranted.

McCormick et al. [9] also reported data showing antioxidant content to have a significant effect on reducing total insolubles (by ASTM D2274)—though only a few data points show this trend as shown in Fig. 7. Biodiesel with high glyceride content (above the ASTM D6571 limit of 0.24%m/m) showed significantly higher levels of insolubles formation than anticipated from the relative antioxidant content, though data points are few. This phenomenon may be due to a mechanism whereby residual acylglycerides react to form oligomers, so that high residual glycerine levels are linked to increased insolubles. McCormick et al. [9] concluded that both total glycerine and antioxidant contents significantly affect insolubles formation and appear to be of similar importance. Limits on residual acylglycerides specified in biodiesel fuel quality standards, such as EN 14214, are therefore important in terms of minimising insolubles formation. However, unlike antioxidant content, high glycerine has no discernable effect on IP, so that measurement of IP does not capture the impact of total glycerine on insoluble formation. Increased insolubles formation that is possibly linked to high glycerine levels is not detectable by the Rancimat method. These phenomena appear to warrant further examination.

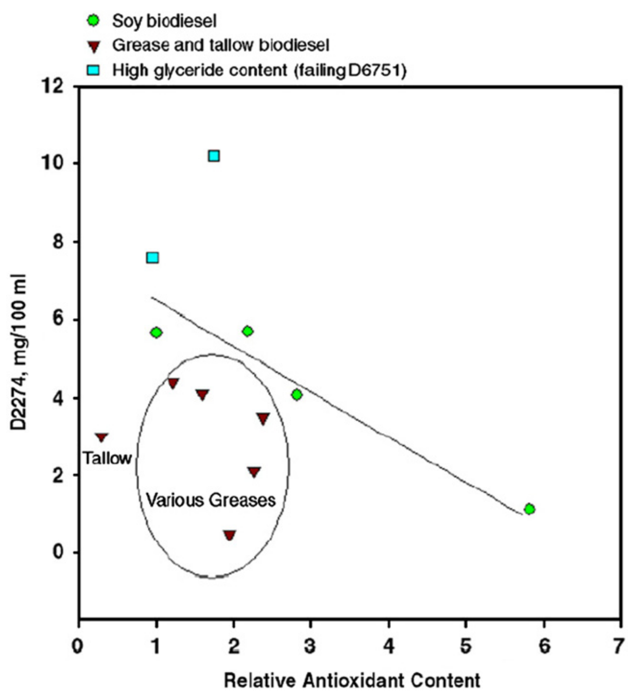


Fig. 7. Total insolubles vs. relative antioxidant content [9].

3. Factors affecting biodiesel oxidation stability

Oxidation stability of biodiesel FAME characterized by Rancimat induction period (RIP) according to test method EN 14112 is affected by various factors including:

- Fatty Acid (FA) composition: the degree of FAME unsaturation, configuration of double bonds, the molecular weight and the relative proportions of different FA present.
- The amount of impurities present, such as metals, free fatty acids, additives and antioxidants.
- Prior exposure of the FAME sample to pro-oxidizing conditions—air, heat, and light.
- Physical parameters of the Rancimat test, such as the sample mass, test temperature and air flow rate, conductivity cell (distilled water) volume.

3.1. *Fatty acid composition*

The FA composition of different oils and fats can vary considerably – see Table 2 – which is data adapted from The Biodiesel Handbook, published by Knothe et al. [18]. Many of the oils and fats listed have been investigated for use as biodiesel. Generally, the FA composition of FAME products derived from vegetable oils or animal fats corresponds to that of the parent oil or fat [5]. The FA composition of FAME is a major factor influencing oxidation. Four feedstocks dominate world-wide biodiesel production: soybean, rapeseed, palm and sunflower [32]. The fatty acid chains of these feedstocks contain primarily 16 or 18 carbon atoms and from zero to three double bonds.

Table 2
Typical fatty acid compositions for various fats and oils [18].

Oil or fat	Fatty acid composition (wt%)									
	8:0	10:0	12:0	14:0	16:0	18:0	18:1	18:2	18:3	22:1
Canola					1.5–6	1–2.5	52–67	16–31	6–14	1–2
Corn				0–0.3	7–17	1–3	20–43	39–63	0.5–1.5	
Linseed					6–7	3–5	13–37	5–23	26–60	
Olive			0–1.3	7–20	0.5–5	55–85	4–21			
Palm		0–0.4	0.5–2.4	32–48	3.5–6.3	36–53	6–12			
Peanut				0–0.5	6–14	2–6	36–67	13–43		0–0.3
Rapeseed				0–1.5	1–6	0.5–3.5	8–60	9.5–23	1–13	5–64
Safflower					5.3–8	2–3	8–23	68–83		
Soybean					2–13	2–6	8–31	49–57	2–11	0–0.3
Sunflower					3.5–7.6	1.3–6.5	14–43	44–74		
Beef Tallow				2–7	25–37	9.5–34	14–50	26–50		

The names of the more common fatty acids listed in Table 2 are as follows:
14:0 Myristic acid (tetradecanoic acid).
16:0 Palmitic acid (hexadecanoic acid).
18:0 Stearic acid (octadecanoic acid).
18:1 Oleic acid (octadecenoic acid).
18:2 Linoleic acid (octadeca-dienoic acid).
18:3 Linolenic acid (octadeca-trienoic acid).
22:1 Erucic acid (docosenoic acid).

Di- and tri- unsaturated fatty acids contain the most reactive bis-allylic sites for initiating the autoxidation chain reaction [9]. Oxidation stability was reported to correlate not with the total number of double bonds, but with the total number of bis-allylic sites [9]. Vegetable oils rich in polyunsaturated linoleic and linolenic acids, therefore tend to give methyl ester fuels with poor oxidation stability [32].

3.1.1. Position of the double bond

Knothe and Dunn [5] compared the oxidation stability (OSI values at 70 and 90 °C) of several high purity, mono-ene methyl ester samples of the same carbon length, and showed that oxidation stability varies according to the position of the double bond. The oxidation stability of 18:1 methyl esters reduced and then increased, as the double bond site changed from the 6th (Δ6) carbon position to Δ9, and to Δ11, respectively. It appears that further investigation is needed to gather further data and to examine the possible causes.

3.1.2. Molecular weight

Molecular weight (MW) of the alkyl-ester chains affects the concentration or density of unsaturation in a given sample. Although, oxidation stability depends more on the nature of the double bonds in a molecule and less on the MW [5]. Consider two (hypothetical) FAME samples of precisely equivalent mass; (i) a sample of pure mono-unsaturated shorter-chain oleic acid methyl ester and (ii) a sample of pure monounsaturated longer-chain erucic acid methyl esters. The oleic acid sample (i) will contain a greater number of molecules, and will hence possess a greater density of unsaturation.

Similarly, the type of alcohol (methanol or higher alcohols) used to make biodiesel can affect oxidation stability by relatively altering the MW of the product alkyl-ester. Knothe and Dunn [5] reported OSI data for various alkyl esters of oleic acid (methyl, ethyl, propyl and butyl oleate). Higher MW esters did exhibit greater stability, though did not follow a clear trend "which bears further investigation".

Work examining the effect of varying MW on oxidation stability was reported by Knothe and Dunn [5]. The oxidation stability of higher MW compounds, such as neat methyl 11-eicosenoate (C20:1) were compared to those of lower MW, such as methyl oleate (C18:1). Higher MW compounds were found to exhibit greater oxidation stability; confirming the prediction that oxidation stability is increased when the concentration of double bonds is lower as a result of the higher MW of the compounds tested. However, the authors [5] commented that more compounds of a similar nature may need to be studied to confirm the prediction.

In summary, if there were a constant number of double bonds per molecule, then increasing MW, for a given mass of sample, would increase oxidation stability. Conversely, with decreasing MW, the concentration of double bonds increases in a given mass of sample and oxidation stability should therefore decrease [5].

3.1.3. Proportions of different FAME

Considering a (theoretical) pure mixture of fatty acid methyl esters, e.g., pure methyl oleate mixed (C18:1) with pure methyl 13-docosenoate (C22:1), it would follow that as the proportion of the higher MW compound increases, the oxidation stability of the mixture should increase, since the concentration of double bonds in a given mass of sample is reduced. Increased oxidation stability of some biodiesel FAME may be attributable to greater proportions of higher MW ester compounds. For example, Rapeseed Methyl Esters, (RME) can contain exceptionally high proportions (5–64 wt%) of erucic acid (22:1) – see Table 2 – which is usually present in only small amounts (< 2 wt%), in many of the other common oils and fats used for biodiesel.

Park et al. [38] examined the effects of blending different biodiesels on the oxidation stability and cold flow properties of the aggregate fuel. Blending more saturated, more stable biodiesel (e.g., palm) with more unsaturated, more unstable biodiesel (e.g., rapeseed) was demonstrated as a method of simultaneously improving oxidation stability of the more unstable FAME, whilst improving the cold flow properties of the more saturated type. Twenty one different blends of palm, rapeseed and soybean biodiesels were compared in the study. The fatty acid compositions of the individual biodiesel samples that were blended together were determined by gas chromatography, which showed the linoleic+linolenic acid contents to be 11%, 30% and 60% (approx) for the individual palm, rapeseed and soybean biodiesels, respectively. Rancimat induction period (h) was measured (EN 14112) at 110 °C, and corresponding with composition measurements, the order of stability was palm (11 h) > rapeseed (6.94 h) > soybean (3.87 h). In terms of cold flow ability, the order was rapeseed (−20 °C) < soybean (−3 °C) < palm (+10 °C). Data presented for various blend combinations of the three biodiesels showed a clear, inversely proportional correlation between induction period (h) and 'linoleic+linolenic content' (wt%), with stability decreasing as linoleic+linolenic content increased as shown in Fig. 8. A trendline is fitted to the data allowing prediction of induction period (h) based on linoleic+linolenic acid (wt%) content. The data correlation demonstrates the clear dependence of biodiesel oxidation stability upon fatty acid composition. Blending different biodiesels to reduce the overall linoleic+linolenic acid content (wt%) is thus a simple yet effective method of improving oxidation stability, that can also be of benefit in terms of cold flow ability. Importantly, the blending technique may enable the commercialization of feedstocks for biodiesel that would otherwise be unsuitable. For example in colder climates like the UK, the poor cold flow properties of palm oil derived biodiesel restricts its use. Blending may be one way to overcome this problem.

Hoekman et al. [39] compared data on the FA compositional profiles of TAG fractions found in algal lipids for various algal strains that have been investigated as potential biodiesel feedstocks. Comparison of algal FA profiles with FA profiles of more well known oils/fats showed similarities, for example considerable amounts of C16 and C18 components in algal species, though these components were not as dominant as in most vegetable oils. Algal FA profiles were broader, containing lighter species (C12–C15) and heavier species (C20–C22). Many algal lipids

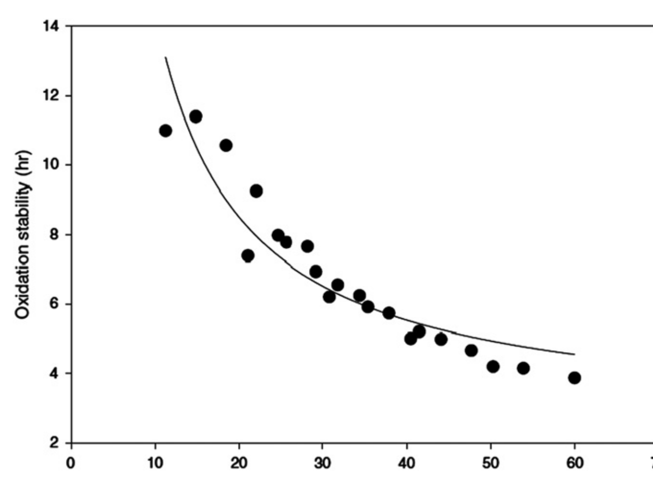


Fig. 8. Oxidation stability of blended biodiesel vs. the content of linoleic (18:2) and linolenic (18:3) acids[38].

contained substantial levels of highly unsaturated species, including FAs with 3 to 6 double bonds, typically Eicosapentaenoic acid (20:5) with levels up to 28%m/m, and also lower levels of Docosahexaenoic acid (22:6). These highly unsaturated species would have important implications with respect to biodiesel properties, such as the IV, CN and oxidation stability. Bucy et al. [40] further investigated the properties of algal-oil derived methyl ester biodiesel, noting the high content of these long chain polyunsaturated fatty acids (LC-PUFA) often present in microalgae species that are suitable for large scale cultivation for biodiesel production. These constituents are problematic in terms of oxidation stability, as well as other properties such as Cetane number. The study results suggested removal of 50 to 80% of the LC-PUFA from the algal oil investigated was necessary for meeting existing specifications on oxidation stability.

3.2. *Presence of impurities*

Just as the parent TAG contains impurities, so too will biodiesel unless high purity samples are especially prepared as in the work by Knothe and Dunn [5]. The nature and amount of each impurity present in biodiesel will vary according to feedstock origin and prior processing. Impurities that are known to affect oxidation stability (RIP) of FAME include: metals, free fatty acids, contaminant peroxides, fuel additives (which may be acidic), and of course antioxidants (those naturally present as well as additives). For commercial biodiesel samples containing various impurities, the correlation of oxidation stability (RIP) with the number of bis-allylic sites may be skewed or overshadowed by these other factors [9].

3.2.1. *Metals*

Biodiesel oxidation studies have confirmed the catalyzing effect of metals on oxidation, with copper showing the strongest effect. Although, the influence of fatty ester structure (especially unsaturation) was even greater [7]. Certain metals, such as Cu, Fe, Ni, Sn, and brass (a copper rich alloy) can increase the oxidizability of fatty acid chains. Copper is known to be generally the worst offender [13]. As little as 70 ppm of Cu in rapeseed oil can greatly increase oxidation. Iron has been shown to be a potent hydroperoxide decomposer, with a more pronounced effect at higher temperature. It has been reported to increase acidity of biodiesel more than copper [13].

Knothe and Dunn [5] examined the oxidation stability (OSI) of methyl oleate in the presence of Cu, Fe and Ni—where Cu showed the strongest catalyzing effect. In other work, PV of biodiesel samples (primary oxidation products) was shown to increase more rapidly in Cu containers, than in steel types. Contaminant-metal particle size, and thickness of oxide coatings are cited as influencing factors. However, the influence of increasing bis-allylic carbons was found to be of greater magnitude than the effect of metals. Hence reduction of highly unsaturated components will likely enhance oxidation stability more than preventing exposure to metals [5].

McCormick et al. [9] analysed the metal contents of 27 commercially available U.S. biodiesels, reporting on Cu, Fe and Zn. Results $A(B)$, where A=no. of samples (of the 27), and B=metal content (ppm), were:

- For Cu levels: 19(0), 5(1), 2(2), and 1(5).
- For Fe: 19(1), 3(2), 2(3), 1(4), 1(9), 1(12).
- For Zn: 12(0), 5(1), 4(2), 2(4), 1(5), 1(6), 1(8), and 1(38).

No correlation was observed between metal content (Cu, Fe, Zn individually or the sum of all three) with either insolubles (ASTM D 2274) or with RIP. However, samples with individual metal concentrations of ≥ 6 ppm exhibited very short IP as well as higher total insolubles > 4mg/100 ml. These particular results infer that poor stability linked to metal contamination may not be a great issue for commercial biodiesel. Metal content is probably linked to the choice of materials used for biodiesel reactor/process vessels, pipework and storage containers; issues which could be further investigated.

Shiotani and Goto [41] investigated the oxidation stability properties of palm oil methyl ester (PME) and aggregate blends with diesel fuel, as well as the influence of fuel tank metal on oxidation stability. PME made from refined and crude palm oils were both examined. Crude PME had much higher oxidation stability (13.0 h) than refined PME (6.65 h), (by the EN 14112 test method) and this was explained by the presence of natural antioxidant beta-carotene in the crude oil. The main components in PME were the methyl esters of saturated palmitic acid ($\sim$40%), mono-unsaturated oleic acid ($\sim$45%), and di-unsaturated linoleic acid ($\sim$12%); explaining the very low (<60) iodine value, and high oxidation stability (>6 h) of PME, although saturated esters also accounted for the poor low temperature performance (CFPP $\sim$10 °C), since saturated fatty compounds tend to congeal at higher temperatures.

The main effect of blending PME with diesel was thus on low temperature performance of the aggregate fuel. The cold filter plugging point (CFPP) of neat diesel was -15 °C, compared to $+10$ °C for neat PME. A blend of 50% PME gave a CFPP of -3 °C. As %PME increased then Rancimat induction period of the aggregate blend decreased. The effect of Rancimat test temperature was also examined for various blends, showing that a 10 °C test temperature increase resulted in approximate halving of the induction period. It was noted that "in modern diesel engines, fuel temperatures are higher due to the use of common-rail fuel injection systems, and it is not uncommon to have fuel temperatures of 140 °C, (so that) oxidation degradation (is potentially a serious issue) when biodiesel is used in common-rail fuel injection systems". Oxidative degradation of Biodiesel is said to be enhanced by temperature, wetted metals and light. In an automotive fuel supply system, many different metals are used and the effects of various metals on the oxidation stability of PME were evaluated in the study; metals including zinc, tin copper, iron, aluminium, and various aluminium alloys. A sample of PME was held in a glass vial at 20 °C with a metal test piece, and the induction period of the sample was tested over several weeks. Oxidation stability was shown to decrease in the presence of all the metals. The order of effect (strongest to weakest) was Copper, tin, iron, zinc, aluminium, with the strongest effect from copper reducing induction period of PME from 13 h down to almost 0 h. Various alloys of aluminium had a stronger effect relative to pure aluminium. Tests were also carried out with PME samples kept in metal test cups (either bonde steel or terne sheet) at 20 °C; samples were either open or closed to atmosphere. In the terne sheet, the Rancimat induction period of the PME sample closed to atmosphere degraded dramatically, falling from >13 to $\sim$0 h in only around 14 days, while the sample open to atmosphere degraded much more gradually, only falling to $\sim$10 h after 50 days. Pitting corrosion of the closed terne sheet cup occurred, thought to be caused by the acids formed (oxidation products), with enhanced corrosion of the closed sample due to "the evaporation of impurities being prevented". The degradation of samples kept in the bonde steel cup (open and closed) was comparatively much lower. This work highlights the importance of fuel system material compatibility with Biodiesel fuels; certain metals will accelerate oxidative degradation of the fuel. Fatty acid methyl ester composition of the PME was also monitored as oxidation proceeded showing that unsaturated components were consumed by the oxidation process; the concentration of linoleate

and oleate decreased, while the level of saturated palmitate (not consumed by oxidation) relatively increased.

3.2.2. Free fatty acids

Free fatty acids have been shown to have a significant effect on biodiesel oxidizability; free carboxylic acids have been found to be far more oxidatively unstable than their corresponding methyl esters [13]. In work reported by Knothe and Dunn [5] free acids have been shown to have lower OSI values than their corresponding esters. This presents a further reason for limiting free acids in biodiesel fuel quality specifications.

3.2.3. Additives

Certain acid corrosion inhibitors, commonly present in No. 2 diesel, have been shown to increase the formation of secondary oxidation products such as polymeric gums, even at only low concentrations—significant for biodiesel blends with No. 2 diesel. Further research is required in this area [13]. Other additives commonly used in biodiesel such as cold-flow improvers may affect oxidation stability and warrant investigation.

3.2.4. Antioxidants

The effects of various antioxidants on biodiesel oxidation stability have been investigated extensively in the open literature [9,16,33,42–47]. Dunn [1] presented a thorough review of such work, not covered in detail here. In summary, synthetic types, such as TBHQ, BHA, BHT and PG are generally more effective than natural types (tocopherols) so are generally preferred commercially. Many commercial additive formulations contain two or more antioxidants [1]. Effective concentrations appear to be between 200–1000 ppm, depending on the substrate and the type of stability test used to evaluate additive performance [46].

Schober and Mittelbach [45] showed that for a good antioxidant such as TBHQ, a 1000 ppm dose can improve biodiesel RIP by a factor of around 2, or even far more, depending on the substrate. Although over-dosing can reduce oxidation stability and in extravagant doses can deleteriously affect other fuel properties. High doses (up to and including 1000 ppm) for several common antioxidants have been shown to have no significant negative effects on other biodiesel properties as defined by EN 14214 [45] with the exception of acid value (mg KOH/g), which increased slightly. Though at a lower (250 ppm) dose, no significant effect was observed. It was thus recommended to use antioxidants at the lowest possible concentrations. It was also mentioned that evaporation of certain antioxidants during Rancimat testing might be an issue that could impact results.

TBHQ was again shown to be one of the most effective synthetic types by Bondioli et al. [48]—an initial dose of 400 ppm in undistilled RME achieved RIP > 32 h after enduring 12 months of storage, compared to undistilled RME without any antioxidant which achieved just under 7 h.

As antioxidants are consumed, their effectiveness reduces and oxidation stability decreases. During the frying of vegetable oils, most of the natural antioxidants are consumed and it is possible to assume poor oxidation stability for biodiesel made from used frying oil [3]. This problem can be solved by adding antioxidants.

Xin et al. [33] investigated the kinetics of safflower biodiesel oxidation, stabilized by the addition of propyl gallate (PG) antioxidant. Doses were varied from 0–5000 ppm. Oxidation stability of the various dosed samples was measured by Rancimat method at temperatures ranging 100–120 °C. For a particular Rancimat test temperature, RIP was shown to increase with antioxidant dose as shown in Fig. 9. At a particular antioxidant concentration, RIP was shown to fall dramatically as Rancimat test temperature increased. Composition and tocopherol content of the un-dosed

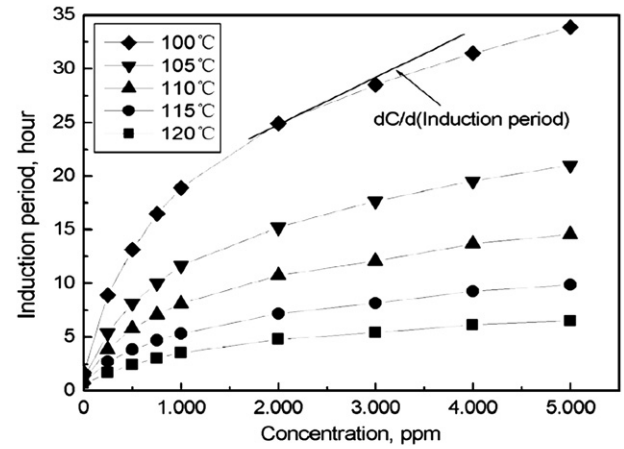


Fig. 9. Antioxidant (PG) concentration vs. Rancimat induction period for safflower biodiesel at various test temperatures. (10 l/h air flow, 3 g samples)[33].

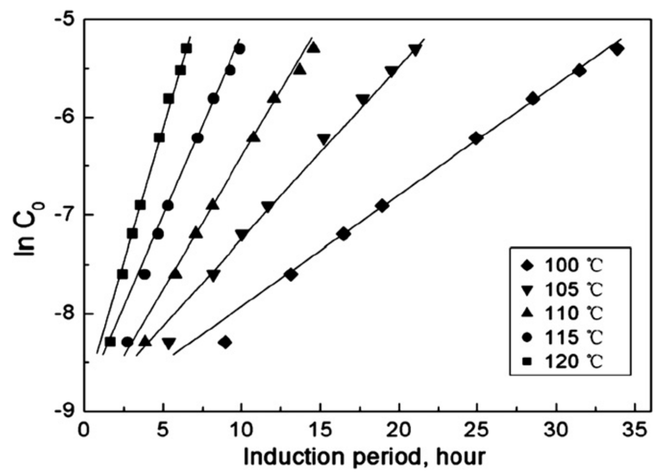


Fig. 10. Rancimat induction period (t_i) of safflower biodiesel vs. the natural logarithm (ln) of initial antioxidant concentration (C_o) for various test temperatures [33].

biodiesel was determined by chromatography (HPLC) method, which revealed highly unsaturated FAME content and relatively low tocopherol content; explaining the consequently very low (0.86 h) RIP of safflower biodiesel. Eq. (18) is a first order rate reaction law proposed by Xin et al. [33]; describing antioxidant-stabilized biodiesel oxidation kinetics.

$$\ln C_o = k(t_i - t_{io}) + \ln C_{cr} \tag{18}$$

where, C_o is initial antioxidant concentration (ppm), C_{cr} is the antioxidant concentration threshold below which the antioxidant has no effect on retarding oxidation (ppm), t_i is the measured Rancimat Induction Period (h), t_{io} is the RIP without synthetic antioxidant addition (h), k is the reaction constant of antioxidant consumption, i.e., when $C_o < C_{cr}$ then $t_i = t_{io}$. Eq. (18) describes a linear relationship between induction period (t_i) and the natural logarithm of initial antioxidant concentration (C_o), at a particular Rancimat test temperature. Equation lines fitted to test data show good correlation as shown in Fig. 10. Gathering of further supporting data with investigation of the sensitivity of empirical coefficients to biodiesel composition and antioxidant type appears warranted.

For biodiesel kept in storage, RIP can be checked periodically and the fuel dosed with antioxidant to recover lost stability as necessary. However, for out of spec fuel (RIP < 6 h), what would be the optimum antioxidant dosage, given that the increase in stability exhibits diminishing returns as dose increases? These

aspects of practical antioxidant application appear in need of further investigation.

The authors Chen and Luo [47] investigated the oxidation stability of biodiesel samples derived from free fatty acids (FFAs), which were dosed with various antioxidant additives (11 types) at different concentrations (between 100 and 1000 ppm). The authors investigated FFA-derived biodiesel, since it has the advantage of not competing with the edible oil market, and as such is an attractive feedstock for biodiesel production. RIP of biodiesel samples was determined in accordance with the Rancimat method (EN 14112), where the RIP of un-additivised FFA-derived biodiesel was initially very low (0.2 h), but was satisfactorily increased by the addition of antioxidants, some of which were more effective than others.

The effectiveness of an antioxidant added to biodiesel was noted to depend on a variety of factors, including the fatty acid profile of FAMEs, the amount of natural antioxidants present, and the storage conditions. All of the antioxidants added at 1000 ppm concentration showed a positive impact on RIP, though the relative improvement in RIP was a function of antioxidant type, which was attributed to their different chemical structures. Generally, Rancimat IP increased with antioxidant concentration, and decreased with higher Rancimat test temperature. The relationship between RIP and the consumption of antioxidant was described by first order reaction kinetics, as reported earlier by Xin et al. [33].

In the study by Chen and Luo [47], the order of antioxidant effectiveness was observed to be: (PY) pyrogallol > Ethanox 4760E > (PG) propyl gallate > Ethanox 4740 > (PDA) *N*,*N*′-di-*sec*-butyl-*p*-phenylenediamine ≈ (BHA) butylated hydroxyanisole > (BHT) butylated hydroxytoluene > (MBMTBP) 2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenol) ≈ TBHQ > (DTBHQ) 2, 5-di-tert-butylhydroquinone > α-Tocopherol. Overall, the study recommended Ethanox 4760E (250–1000 ppm), which compared to PY and PG showed better solubility. PY and PG also slightly increased the acid value of biodiesel.

The natural logarithm of RIP showed a linear relationship with the test temperature, so that RIP measured at higher temperatures could be extrapolated to estimate the biodiesel storage life at lower storage temperature. Results suggested that an RIP > 6 h (measured by EN14112 method) may infer at least a 6 month storage life, although it would appear further study is warranted to confirm this.

Samples of biodiesel were stored for 6 months and fuel properties (RIP, acid value, kinematic viscosity) were monitored. The biodiesel samples dosed with antioxidant showed little or no deterioration in these properties whilst the un-dosed sample changed more dramatically. Acid value and viscosity increased as a consequence of oxidation, while RIP reduced with storage time.

Obadiah et al. [49] investigated the effects of various antioxidants on the storage stability of Pongamia pinnata (karanja) derived methyl ester biodiesel. Storage stability studies were carried out according to ASTM method D4625 under two different storage conditions: 30 °C for 50 weeks, and 43 °C for 12 weeks. Karanja biodiesel samples of 200 ml were stored in open-to-air 250 ml glass bottles. Kinematic viscosity (KV) and acid value (AV) of samples were monitored. Individual samples were dosed with a particular concentration of antioxidant (0, 500, 1000, 2000, or 3000 ppm). Five different antioxidants were tested: BHT, BHA, PY, Gallic acid (GA), and TBHQ. RIP of samples was measured at 110 °C test temperature. Initial RIP of the karanja biodiesel was 0.33 h.

PY performed best (showed greatest efficacy); which increased RIP to 25 h at 2000 ppm, and 34 h at 3000 ppm. GA performed worst; it did not increase RIP above 0.88 h at 3000 ppm.The other antioxidants performed similarly, increasing RIP to approximately 5–6 h at 3000 ppm.

The storage stability study results showed that for all samples, KV and AV significantly increased with storage time. However, samples loaded with more (of the respective) antioxidant showed relatively smaller increases in KV and AV, so that a higher concentration of antioxidant better suppressed oxidation progression. Results indicated that PY and TBHQ better suppressed oxidation progression, compared to the other antioxidants. PY was concluded to be the best antioxidant overall.

Kivevele et al. [50] studied the effects of synthetic antioxidants on the oxidation stability of methyl ester biodiesel produced from Croton Megalocarpus oil, of African origin. Oxidation stability was also determined by the Rancimat method, (as well as other properties of the biodiesel, not further discussed here). It was found that RIP of the un-dosed biodiesel (4.04 h) did not meet EN 14214 specification (> 6 h). However, antioxidants were effective in improving RIP. Three antioxidants were tested: PY, PG and BHA, dosed at 200, 500 and 1000 ppm, respectively in separate tests. As expected, it was observed that RIP increased with the antioxidant dose.

RIP results when BHA was added were 4.77 h (200 ppm), 5.48 h (500 ppm), 7.67 h (1000 ppm). Likewise for PG, results were: 7.59 h (200 ppm), 15.2 h (500 ppm), 20.5 h (1000 ppm). For PY: 12.1 h (200 ppm), 15.7 h (500 ppm), 21.7 h (1000 ppm). Hence results showed antioxidant efficacy was in the order PY > PG > BHA.

Thermal stability was determined using a TGA 2050 Thermogravimetric Analyser, where biodiesel samples (5–8 mg) were purged with oxygen and heated to 500 °C at a ramp rate of 10 °C/min. When severe oxidation was initiated, removal of secondary oxidation products caused rapid sample weight loss (measured by the instrument) indicating the onset temperature of thermal oxidation, which is an indicator of sample thermal stability. Although no thermal stability limit is specified as yet for biodiesel in any fuel quality standard. The un-dosed biodiesel recorded an onset temperature of 211 °C. The effect of antioxidant on the onset temperature was not clearly established, though there was a slight increase in onset temperature recorded for the sample dosed with PY: 500 ppm (218 °C) and 1000 ppm (217 °C).

Araujo et al. [51] investigated a novel, new electro-analytical technique for determination of TBHQ levels in soybean biodiesel samples. Method results were compared with TBHQ determinations carried out by high performance liquid chromatography (HPLC) measurement, which showed the results obtained from the new method were satisfactorily precise. Advantages of the technique were reported to be faster analysis, lower cost, more straightforward and adequately sensitive to TBHQ levels, compared to other methods such as HPLC. It was thus suggested as being suitable for routine quality control of TBHQ levels in biodiesel samples.

3.3. Mass and viscosity of the sample under test

Knothe and Dunn [5] examined the oxidation stability (OSI) of methyl oleate and triolein (the TAG of oleic acid) for samples of varying mass (in the range 2–8 g). A downward trend in oxidation stability was observed with increasing sample mass. This was attributed to the greater number of double bonds present in the sample; a greater mass of sample contains a greater number of allylic positions available to react with oxygen. Thus careful weighing of samples for accelerated oxidation tests is important.

In the same study [5], the effect of sample viscosity on oxidation stability (OSI) was examined. The more viscous TAG of oleic acid (triolein) was shown to exhibit greater oxidation stability than methyl oleate. It was explained that viscosity can affect: the mass-transfer of oxidation products to the air–oil interface, how fast bubbles traverse the sample, the size of bubbles, and the rate at which oxygen from the bubbles dissolves into the sample. Hence more viscous samples may yield higher

Table 3
Reported BAPE and APE values of methyl esters [35].

Methyl ester	APE	BAPE
SME	–	66.5
UCOME	146.2	28.4
MO	200	0

oxidation stability. Biodiesel viscosity is increased as a consequence of incomplete transesterification, where unreacted mono- di- and tri-acylglycerides remain in the fuel as impurities.

3.4. Effects of temperature on oxidation stability

Dunn [35], examined the effects of temperature (T) on the Oil Stability Index (OSI) of Soybean oil fatty acid methyl esters (SME) and used cooking oil fatty acid methyl esters (UCOME), which were compared to pure methyl oleate (MO). Increased OSI block temperature (T) accelerated the oxidation reaction and decreased OSI. Modelled as a function of T, ln(OSI) vs. T^{-1} showed a linear correlation, though the relationship was said to be unreliable at $T<50$ °C. At constant T, SME yielded lower OSI than either UCOME or MO. This was explained by the correlation of OSI with values of bis-allylic position equivalents (BAPE) and allylic position equivalents (APE), values of which were examined for the methyl esters. Table 3 summarizes the reported BAPE and APE values. Higher BAPE value indicated greater susceptibility to oxidation; hence explaining the lower OSI of SME. UCOME had a higher BAPE than MO. However MO had a much higher APE value than UCOME. Bis-allylic positions are around 2.5 times more reactive than allylic positions [1], so that the reactivity (and OSI) of MO might be expected similar to that of UCOME. However, this was not the case; UCOME yielded significantly higher OSI than MO despite having comparable IV. The likely explanation was said to be the possible presence of antioxidants in the UCOME, compared to zero antioxidant in the pure MO. Dunn [35] reported that the presence of antioxidants in FAME causes the slope of Arrhenius plots to decrease relative to uninhibited FAME. Work by Frankel [20] explained this occurrence, since the effect of antioxidants is to increase the activation energy of oxidation. Hence the effectiveness of antioxidants increases as temperature decreases. Conversely, as temperature increases antioxidant efficacy decreases and at a given elevated temperature, the effect of antioxidants vanishes and may even act as pro-oxidant. This means that Biodiesel FAME protected with added antioxidants, will lose that protection at sufficiently high temperature. This behaviour may well be important in modern common-rail fuel systems where fuel can encounter high temperatures.

Dunn [35] examined the effect of T on OSI by the application of two mathematical models: ln(OSI) vs. T and ln(OSI) vs. T^{-1}. Both models showed a linear correlation for the experimental data obtained, allowing estimates of OSI as a function of T. Eq. (19), modelled the correlation of ln(OSI) vs. T^{-1} with regression coefficients B_0 and B_1:

$$\ln(\text{OSI}) = B_0 + B_1 T^{-1} \tag{19}$$

Kinetic parameters for the oxidation reaction, such as the activation energy E_a, were further quantified based on first-order kinetics. The degree of conversion was defined (α)—the % of oxidized substrate. The early stages of oxidation typically follow first-order reaction kinetics [35], so the rate that the degree of conversion increases may be expressed by Eq. (20):

$$\frac{d\alpha}{dt} = k(1-\alpha) \tag{20}$$

where t=reaction time, k=the reaction coefficient. Rearranging and integrating from t_0 to t^* and from 0 to α^*, where t^* and α^* are defined as the time and degree of conversion corresponding to the induction period for oxidation (i.e., t^*-t_0=OSI) – see Eqs. (21) to (24):

$$\int_0^{\alpha^*} \frac{1}{(1-\alpha)} d\alpha = k\int_0^{t^*} dt \tag{21}$$

$$-\ln(1-\alpha^*) = k(t^*-t_0) = k(\text{OSI}) \tag{22}$$

if,

$$\vartheta = -\ln(1-\alpha^*) \tag{23}$$

then,

$$\text{OSI} = \frac{\vartheta}{k} \tag{24}$$

For a given FAME, α^* is a constant at a particular temperature where OSI is analyzed, hence ϑ is also a constant. The rate of oxidation is exponentially related to temperature, and consequently k is dependent upon T and is generally expressed by the Arrhenius relation—Eq. (25):

$$k = Ze^{-E_a/R_g T} \tag{25}$$

where Z=the frequency factor, E_a=the reaction activation energy, R_g=the gas constant.

Substituting Eq. (25) into (22), gives Eq. (26):

$$\text{OSI} = \frac{\vartheta}{Ze^{-E_a/R_g T}} \tag{26}$$

Taking natural logarithms gives Eq. (27):

$$\ln(\text{OSI}) = \ln\frac{\vartheta}{Ze^{-E_a/R_g T}} = \ln\vartheta - \ln\left(Ze^{-E_a/R_g T}\right) = \ln\vartheta - \ln Z + \left(\frac{E_a}{R_g}\right)T^{-1}$$

$$\ln(\text{OSI}) = \ln\left(\frac{\vartheta}{Z}\right) + \left(\frac{E_a}{R_g}\right)T^{-1} \tag{27}$$

Regression coefficients of Eq. (19) can be compared with Eqs. (27) giving (28):

$$B_0 = \ln\left(\frac{\vartheta}{Z}\right) \quad B_1 = \left(\frac{E_a}{R_g}\right) \tag{28}$$

hence regression coefficients may be used to calculate activation energy E_a (kJ/mol) and the characteristic ratio=e_0^B. Dunn [35] calculated E_a and e_0^B for each of the FAMEs tested. E_a was 90, 82 and 106 (kJ/mol) for SME, MO and UCOME, respectively. Dunn [35] calculated regression coefficients and kinetic parameters for SME, UCOME and MO and extrapolated the developed models to estimate OSI at a lower temperature of 50 °C. The estimates reportedly agreed well with OSI measured at that temperature, so that extrapolation was reliable. However, extrapolation to reasonable storage temperatures "was more problematic". At 30 °C, model A predicted 99, 7180 and 1520 h for SME, UCOME and MO, respectively, whilst model B predicted 160, 19,100 and 2650 h, respectively. It was concluded that estimates decreased in reliability as the temperature moves further away from the temperature range employed to develop the models.

3.5. Processing and storage conditions

After biodiesel is exposed to pro-oxidizing conditions, oxidation stability is worsened. Such conditions can occur during manufacture, handling and storage. Pro-oxidizing parameters which have been investigated include exposure to air, heat, light and metals; influenced by the nature of the storage container. Generally, the presence of air and elevated temperatures facilitate oxidation [7], as does the presence of peroxides or metals (radical initiators) [16]. Oxidation can be catalyzed by exposure to light, but such photo-oxidation should not be significant for the manufacture and

transport of biodiesel fuel [13]—true so long as the exposure of biodiesel to strong light sources is minimal i.e., it is handled and stored in opaque containers. As a test to confirm these general observations, two identical biodiesel samples can be kept under different conditions; one exposed to more oxidizing conditions (higher temperature, oxygen, light); the other kept refrigerated in an air-sealed container in darkness. After prolonged storage, the refrigerated sample shall exhibit improved oxidation stability (longer RIP). Relatively increased levels of oxidation products would be present in the unrefrigerated sample, and its physical properties would be more substantially altered. However, a method for storage stability prediction (prediction of future RIP value based on storage conditions) has not yet been established—scope for such development has been noted [11,18,48].

Bondioli [48] studied stability under commercial storage conditions over one year. Eleven biodiesel samples derived from various feedstocks and manufacturing processes (distilled and non-distilled) were prepared, some with antioxidant additives, and each was stored in a 200 l drum. Fuel properties of each were periodically analysed and ambient storage temperatures monitored. One drum was stored outdoors and shaken occasionally; promoting biodiesel/air mixing—and only this sample recorded increased acidity and polymer levels. The 10 other 'steady' samples showed no significant changes in these and several other fuel properties. However, all samples showed clear increases in PV—levels peaked and dropped in some cases, indicating hydroperoxide degradation with probable formation of secondary oxidation products. In other cases PV levels reached a plateau. Kinematic viscosity (KV) of all samples recorded slight increases, though "did not appear to be a significant parameter for evaluation of storage behaviour". Distilled samples showed comparatively lower KV throughout, "probably because of the near complete removal of non-methyl ester materials such as glycerides" [with higher boiling points than methyl esters]. Only in one case was the maximum EN 14214 specification limit for KV (5.0 mm^2/s) exceeded—after 12 months of ageing for tallow derived biodiesel. RIP measurements showed the largest changes—decreasing with age for all samples. It was observed that two samples having initially comparable RIP, would not necessarily exhibit similar deterioration in RIP. The outdoor, agitated drum exhibited the most dramatic decline in RIP, compared to other initially identical samples. The study results inferred that poor oxidation stability can be induced by incorrect storage conditions; contact with air and agitation must be avoided. Tocopherol content showed little variation in most samples with notable exception for the outdoor stored sample which showed a dramatic drop. Ambient storage temperatures were monitored and were found not to have a large influence on FAME quality at temperatures below 30 °C. However, proper long term study of storage stability sensitivity to temperature variation would require control of sample temperature.

Storage temperature strongly affects the trends seen in oxidation parameters. Elevated temperatures (e.g., ~40 °C) have been shown to hasten decreases in RIP, whilst PV, TAN, viscosity, and polymer levels increase. At ambient or colder temperatures, RIP decreases more slowly, whilst PV, TAN, viscosity, and polymer levels either plateau or increase only modestly [13]. If the same cold biodiesel is agitated (increasing oxygen exposure) then RIP dramatically decreases over time, whilst other variables only change slightly. At very high temperatures (~180 °C), PV remains low due to rapid hydroperoxide decomposition, though secondary products greatly increase; indicated by TAN and viscosity.

Leung et al. [17] investigated biodiesel oxidative degradation under different storage conditions. Experimental results suggested that high temperature, together with air exposure greatly increased biodiesel degradation rate, whilst high temperature or air exposure alone had little effect. This implies more effective biodiesel storage can be achieved by filling opaque storage containers completely with fuel and properly sealing them; minimizing air contact with the fuel, whilst also storing containers in cool, ideally dark environments. The effect of water contamination in biodiesel; leading to hydrolytic degradation of esters to alcohol and free acids was found to be small compared with the degradation effects of air and temperature.

Bouaid et al. [3] studied the storage stability of biodiesel derived from vegetable and used frying oils over a period of 30 months. Methyl esters of high oleic sunflower oil (high, 0.69% and low, 0.10% moisture content), high and low erucic content *Brassica carinata* (Ethiopian mustard) oil, and used frying oil were stored at room temperature in air-sealed, glass containers that were clear and coloured; varying the exposure of contents to light. Properties including: AV, PV, viscosity, IV, and insoluble impurities were measured monthly. Results showed that AV, PV, viscosity and insolubles increased while IV decreased with ageing during storage. Samples exposed to daylight tended to degrade at a faster rate, indicated by PV and AV. Increased moisture content within the sunflower oil esters appeared to promote degradation. The authors called for more detailed study of parameters that affect biodiesel oxidation stability, such as temperature, light, air contact and other parameters.

3.6. Approaches for delaying biodiesel oxidation

Even when taking appropriate precautions, oxidation can only be delayed and not completely prevented. However, several approaches to minimize oxidation of biodiesel fuels are apparent; many of which have already been successfully applied to biodiesel:

- Feedstock oil can be selected to contain low proportions of polyunsaturated FA—although choice is constrained by cold flow performance. Methods that reduce fatty acid chain unsaturation, such as fractional crystallization or hydrogenation have been shown to increase oxidation stability [23], though are usually unsuitable for application to biodiesel due to the added cost, complexity and resulting conflict with other important fuel properties, e.g., cold-flow ability. Different types of FAME can also be blended in order to improve aggregate fuel properties.
- Increasing the content of impurities that worsen oxidation stability should be avoided: metals (Cu, Fe, Ni, Sn, and brass), free fatty acids, peroxides, and certain fuel additives. Materials used for pipework, process vessels and storage containers could affect impurities. Water contamination, perhaps by build-up of condensation, can lead to hydrolytic degradation of esters to alcohol and free acids.
- Clean, dry storage containers should be used and biodiesel exposure to pro-oxidising conditions should be minimized:
    - Exposure to air can be reduced by completely filling, properly sealing and perhaps evacuating storage containers, ideally under an inert gas atmosphere. Storage under an inert nitrogen atmosphere has been used to retard oxidation in FAME and fatty acid ethyl esters of sunflower seed oil for storage at temperatures up to 50 °C [1].
    - High temperatures should be avoided, preferably storing fuel in cool or perhaps even refrigerated environments. The size and shape of the container, as well as how full it is kept will affect biodiesel air exposure and thermal behaviour.
    - Exposure to strong light sources can be avoided by using opaque storage containers kept in darkness, or at least under shade.
    - Agitation promoting biodiesel/air mixing can be minimized by careful and minimal storage container handling.
- Periodic monitoring of fuel quality parameters: RIP, PV, viscosity, insolubles, antioxidant content with remedial action as necessary (e.g., blending or antioxidant dosing).
- Antioxidants can be added to delay oxidation, which will be consumed. Antioxidants are one of the most promising and

cost effective approaches [1] because existing storage tanks and fuel handling systems are more easily used without requiring upgrades or re-design.

3.7. Review of further studies into biodiesel oxidation

Lapuerta et al. [21] evaluated the oxidation stability (RIP) of three different biodiesels, made, respectively from animal fat, used cooking oil (UCO) and soybean oil. RIP was measured for each biodiesel according to the Rancimat method (EN 14112) at 5 different test temperatures (110 to 130 °C in 5 °C steps), and also at different concentrations of the antioxidant additive BHT (ranging from 0 to 30,000 ppm). Results showed that more saturated biodiesel made from animal fats exhibited much higher RIP, which recorded 16 h without additive (at 110 °C). Although it was observed that the unsaturation degree alone was insufficient to explain the effect of the raw material. UCO exhibited reduced stability, probably due to contaminants and loss of natural antioxidants. Low concentrations (1000 to 2000 ppm) of BHT antioxidant additive resulted in large increases in RIP (to around 33 h). Whereas for the two more unsaturated biodiesels (UCO, Soybean), more BHT (3000 ppm and ~1500 ppm, respectively) was needed to increase Rancimat IP at 110 °C to above 8 h. Results showed the strong effect of test temperature and antioxidant concentration on RIP, where lower temperature and higher concentration dramatically increased RIP. Induction period was severely decreased as the test temperature was increased, which made the effects of antioxidant addition at high test temperature difficult to observe. RIP was therefore much more obviously sensitive to the BHT additive at lower test temperature.

As test temperature was increased, much larger concentrations of BHT were needed to maintain the Rancimat induction period above 8 h. For example, the two unsaturated biodiesels (UCO and soybean), required 33,000 and 20,000 ppm BHT to obtain 9.6 and 8.1 h, respectively, at 130 °C test temperature. The authors noted such high concentrations of antioxidant would not be economically or technically feasible for the biodiesel industry and would impair fuel purity (ester content, carbon residue, total contamination).

In light of these findings, the current ASTM (3 h) and EN14214 (6 h) RIP limits were discussed [21], since these limits are being questioned and modifications are expected in future. An increase of the EN14214 limit to 8 h is apparently already approved for the next version of EN14214. There has been suggestion that, because modern fuel injection systems work at higher pressure and temperature than older ones, the test temperature specified by EN14112 should be raised from 110 °C (e.g., to 130 °C). However, the results of the authors [21] presented a case that such a change is unfeasible, due to the accuracy of the RIP determination being reduced, where in particular the sensitivity of the RIP result to significant changes in additive antioxidant levels is lost. Also, achieving current limits for RIP at higher temperature would imply the use of huge amounts of additives. For example, at higher temperature some synthetic antioxidants can be lost by evaporation during the test due to their higher vapour pressure.

The present author [52] recently investigated RIP measurements by the Rancimat method (standard method EN 14112) for a range of biodiesel Fatty Acid Methyl Ester (FAME) samples made from different vegetable oil feedstocks: Sunflower, Rapeseed, Cold-pressed Rapeseed, Palm, Groundnut, Sesame, Grapeseed, Corn, Soyabean, Olive, Coconut, Jatropha, Used Cooking Oil, and two further FAMEs were made from animal fats: Lard and Tallow. Respective fatty acid compositions were also measured by Gas Chromatography (method EN 14103). Fatty acid composition data was used to calculate stability indices known as APE, BAPE, and OX that are intended to characterize the susceptibility of FAME to oxidation. However, lack of correlation between these stability indices and RIP suggested none of them were a good indicator of RIP as measured by the Rancimat method. Correlation was significantly skewed, probably by the presence of residual antioxidant in the samples. Four of the FAME samples (Palm, Olive, Soyabean, and Jatropha) were dosed with antioxidant additive (tertiary butyl-hydroquinone, TBHQ) in order to assess RIP response. Results suggested that a threshold antioxidant dose must be exceeded before the antioxidant had significant effect on retarding oxidation, and also that FAME containing greater levels of polyunsaturated fatty acids exhibited a reduced response (reduced improvement in RIP) to the same antioxidant dose.

Rancimat IP was further measured at discrete test temperatures for two FAMEs (Sesame and Rapeseed). As expected, RIP measurements exhibited Arrhenius temperature dependence. Each Arrhenius curve was extrapolated to estimate the storage life at 40 °C. The result for Sesame was ~1000 h, for Rapeseed ~350 h; inferring if samples were kept at 40 °C they should endure this time before onset of oxidative degradation. To test this idea, the FAMEs were stored at 40 °C for over 100 day. Viscosity and acid value were monitored to indicate signs of oxidation; noticeable increases occurred after ~500 h for Rapeseed. Sesame endured >2000 h before increases occurred, hence the predictions were conservative. Further investigation of the accuracy and utility of such predictions is needed.

Almeida et al. [53] investigated the effects of TBHQ on the storage stability and corrosiveness of biodiesel contaminated with copper. TBHQ was used in the study since the authors reported from their survey of the literature that TBHQ has proven superior antioxidant activity in application to biodiesel. Copper was selected since it is understood to be the strongest metal catalyst for oxidative degradation. The corrosion process of biodiesel kept in fuel containers was simulated by static immersion tests of UCO-derived biodiesel samples, in which a strip of copper was immersed in 30 ml of the biodiesel, held in an amber glass flask, in accordance with ASTM method (G31-72). This was performed for samples with (5000 ppm) and without TBHQ added. RIP and the concentration of copper (by electro analytical method) were measured after 24, 36, 48, 96 and 168 h of static immersion.

Results showed that RIP was dramatically reduced after only 24 h of immersion; RIP of the sample (without TBHQ) reduced from 6.79 to 1.32 h, and RIP of the sample with TBHQ reduced from 24.0 to 2.42 h, where RIP of both of the copper contaminated samples continued to decline thereafter to nearly zero. RIP of the control samples (without copper, but with and without TBHQ) were practically constant over 168 h. Thus exposure to copper caused rapid degradation of RIP.

The concentration of copper was seen to increase in the copper-exposed samples with exposure time; indicating a continuous corrosion process, though the increase was much slower in the sample with TBHQ added. This presented clear evidence that TBHQ retarded the copper corrosion process and acted as corrosion inhibitor through the formation of a protective film layer. However, it was noted TBHQ did not significantly retard degradation of RIP in the copper exposed samples.

The authors proposed that TBHQ molecules absorb on the copper surface and TBHQ is catalytically oxidised to *tert*-butylquinone (TBQ), since TBQ was detected (by mass spectrometry) in the TBHQ dosed sample after degradation had occurred. Mass spectra also gave clear evidence of formation of new high molecular weight molecules, formed by reaction between TBQ radicals and free radicals of long-chain molecules (fatty acid derivatives). Hence it was observed that TBHQ can react with long-chain molecules, leading to the formation of high molecular weight species.

The importance of metal-catalysed degradation of biodiesel was emphasised by the study, since trace metal contaminants can be introduced into biodiesel during storage and handling e.g., from corrosion of metal storage containers and automotive materials; the degradation effect being dependent on the size (or surface area) of the contaminating metal. As long as the biodiesel is exposed to pro-oxidative conditions such as contact with a metallic container, degradation of biodiesel will occur.

Karavalakis et al. [31] investigated the oxidation stability of different biodiesel blends with petro-diesel. Nine different FAME types were blended with four different petro-diesel (PD) fuels, of varying composition. Two of the PDs (referred to as D-1 and D-2) were low sulphur (<50 ppm), the other two PDs (D-3 and D-4) were ultra low sulphur (<10 ppm). Two of these PD fuels (D-1 and D-4) were also noted to contain cracked components (middle distillate fuel extenders), whereas D-2 and D-3 were hydro-treated straight run atmospheric gas oils. The nine FAMEs were of various origin and composition. For example, one contained 65% rapeseed oil and 35% UCO; another was 20% palm, 36% UCO, 44% soybean.

A large number of different blends (1 6 8) were produced (2, 3, 4, 5% 7 and 10 vol%); representative of diesel marketed in the EU. Oxidation stability (RIP) of fuel samples was determined by the Rancimat method. Method EN 14112 was used to evaluate pure biodiesel samples, whilst modified method EN 15751 was used to test blends. RIP of each of the pure biodiesels (B) was measured twice (3 weeks apart). First run RIP results (hours) were: B8 (18.57) > B4 (17.38) > B6 (9.74) > B9 (8.75) > B5 (7.99) > B3 (6.59) > B2 (5.72) > B7 (3.81) > B1 (3.51). After 3 weeks of storage, RIP values had dropped: B8 ($\sim$12) > B4 ($\sim$10) > B6 ($\sim$8) > B9 ($\sim$8) > B5 ($\sim$7) > B3 ($\sim$4) > B2 ($\sim$5) > B7 ($\sim$3.5) > B1 ($\sim$3). The relative age (freshness) of biodiesel and the quantity/type of antioxidant previously added were acknowledged to be strong factors determining biodiesel RIP. The authors reported that results indicated an inverse relationship between RIP and the unsaturated fatty acid content. However, this assertion appeared less clearly evidenced since no supporting plots were presented, e.g., showing correlation between recognised (compositional) stability indices and RIP. Measurements for C18:3 FAME also appeared to be absent from the measured FAME composition data.

RIP results for the biodiesel blends with PD showed that in all (28) cases, as biodiesel content was increased, then RIP of the blend was decreased. When D-1 and D-2 were blended with the least stable biodiesel (B1), then RIP of the blend was correspondingly the lowest, relative to the other blends. RIP failed to meet the EN 590 requirement (>20 h), only for blends of D-1 and D-2 with B1, above 5% blend level. When blended with D-1, RIP results indicated the following order of stability: B6 > B9 > B3 > B2 > B4 $\approx$ B5 > B1. Interestingly, this relative order of stability changed when the same biodiesel blend ratios were prepared using D-2; so that the composition of the PD was observed to affect the overall stability of the blend.

When ultra low sulphur PDs (D-3 and D-4) were blended, again, the relative order of stability was altered. Most of the *ultra* low sulphur PD/biodiesel blends showed lower stability compared to the corresponding low sulphur blends. This was attributed to the presence of sulphur compounds which act as natural oxidation inhibitors.

Two of the biodiesels B3 and B9 (which when blended with low sulphur PDs showed relatively high stability) when instead blended with the ultra low sulphur PDs, their relative stability was much lower, indicating synergistic blend effects. RIP failed to meet the EN 590 requirement (>20 h), for blends of D-3 with B3 and B9 above $\sim$7% blend level.

Furthermore, blends prepared with the ultra low sulphur D-3, and low sulphur D-2 were observed to be relatively more stable than blends prepared with ultra low sulphur D-4 and low sulphur D-1. The authors suggested this was probably related to the presence of cracked stocks (olefinic components) present in D-4 and D-1, which possess lower stability than straight run distillates.

The study by Karavalakis et al. [31] thus presented clear evidence that the composition of the base diesel fuel significantly determines the stability of the resulting biodiesel blend. Results also showed that any antioxidant added to biodiesel strongly affects the stability of the final blend. The authors concluded further work is necessary to better understand the factors and mechanisms which affect the oxidation stability of biodiesel/petro-diesel blends. Without this understanding, confidence in fuel reliability is diminished, particularly if there is large unexpected variation in the properties of biodiesel blends.

4. Impact of biodiesel oxidation on diesel engines

The severity of biodiesel oxidation effects on diesel engine equipment is not well documented. In 2005, Waynick [13] reviewed relevant fuel pump, injector and vehicle fleet tests available in the open literature and commented that very little actual controlled diesel equipment test work had been reported. In the few tests reported, there were consistent sub-catastrophic problems; characterized by increased deposition on injectors and pump parts, increased pressure drops across filters, and a few failed injectors and pumps. One questionable study that was discussed, linked high fuel acidity to problems of increased filter pressure drops, as well as increased varnish/deposits on pump parts observed upon disassembly. However Waynick commented that the problems were likely instead attributable to the high levels of glycerine and acylglycerides that were found in the fuel, which are well known to cause severe engine deposits, rather than high acidity being the cause [13].

In terms of fuel injector coking tendency, greater coking has been noted with biodiesel use compared to low sulphur No. 2 diesel fuel, with RME showing higher coking levels [13]. Though the question of whether or not oxidation of biodiesel might exacerbate coking, perhaps by increasing the fuel viscosity, appears not to have been examined. Another study found increased deposits on fuel pump parts and corrosion in some fuel injector parts when running low stability fuel. A different study found "serious deterioration of fuel injector performance and piston-ring damage… with almost no fuel atomization after 1000 hrs", from running on a B20 blend, although no conclusions on the cause were made. A similar study found premature pump failure after 650 h of running a B20 blend; attributed to fuel pump deposits and filter plugging. Analysis of deposits reportedly showed presence of fatty acid esters and carboxylic acids as well as carboxylic acid salts [13]. In other fuel injector tests, significantly worse deposits were found after running B20 compared to either neat biodiesel or neat petro-diesel [13]. It seems more problems may be encountered when running blended fuels and this appears consistent with other studies, which have observed increased insolubles formation after blending biodiesel with petrodiesel. Biodiesel is miscible with petrodiesel in all ratios [18]. However, biodiesel insoluble species are better kept in solution in neat biodiesel. This antagonistic effect is said to be driven by the lower solvency of petroleum fuels [13]; attributed to biodiesel being highly polar—increasingly so with oxidation, and petro-diesel in contrast, being non-polar. When oxidised biodiesel is blended with petro-diesel, previously soluble species can be expected to precipitate out of solution. No. 1 diesel has even less solvency than No. 2 diesel fuel, so the effect will be even more pronounced—and this is borne out by relevant study results [13]. Ultra-low sulphur diesel fuel has further reduced solvency, exacerbating the problem. Insolubles formation, fuel filter plugging and engine deposit formation related

to biodiesel oxidation may then be worsened by the blending of biodiesel with petro-diesel. Studies in this area are limited so that further work is required to explore this behaviour [13].

There is a further absence of study test results in the open literature examining the tendency of biodiesel to form deposits on hot metal surfaces under dynamic conditions. Limited Jet Fuel Thermal Oxidation Test (JFOT) results have been collected, which involve passing fuel across a heated metal tube (usually 260 °C). Qualitative deposits on the tube are usually rated visually at the end of the test. However, the relationship between biodiesel oxidation and deposit forming tendency has not been established [13].

The BIOSTAB project [11] investigated the effects of biodiesel fuel stability during fuel usage. Automotive bench tests (500 h) and on-road fleet trials (4 cars, 21,000 to 60,000 km per vehicle) of biodiesel of varying stability (high 14–18 h RIP, standard 6 h RIP and low 1.8–3.5 h RIP) demonstrated normal fuel system and engine functionality, even for low stability fuel. The fuels were tested long term in 3 different modern injection systems: a heavy-duty common rail, a passenger car common rail, and a passenger car with a distribution pump fuel injection system. Wear and sedimentation were found to be normal for respective test runtimes. Swelling of elastomers was in found in a distributor pump. Slight oxidation and fuel deposits were found on a fuel injector pump. One fuel filter blocked and some had to be changed in winter. Although no severe problems were reported, even when running with low stability fuel, it was recommended that EN 14214 specification limits on stability should be met to avoid problems "under sharp conditions". A general conclusion on the performance of low stability biodiesel could not be drawn; a more extensive fleet test covering all field influences was said to be required.

In 2007, the Joint Fuel Injection Equipment Manufacturers (Delphi, Bosch, Siemens, Denso, Stanadayne) issued a Common Position Statement regarding the use of FAME [10]. The statement discussed issues particular to FAME fuels that are of concern to fuel system OEMs. Reduced oxidation stability was said to be of major concern as the products of fuel ageing can be potentially harmful to the fuel system. Tests have shown that fuel deterioration can take place in the fuel supply chain and in the vehicle fuel system. The products of oxidative ageing have been shown to be corrosive and polymerization products formed can drop out. Corrosive organic acids (e.g., formic and acetic) can cause corrosion of metal parts, whilst polymerization products cause deposits and precipitation from fuel blends, leading to filter plugging and lacquer formation by soluble polymers in hot areas. Consequently the FIE Industry considered it as essential that blends of 5 percent biodiesel (conforming to EN 14214) with petrodiesel (conforming to EN 590), known as EU-B5, should achieve an RIP ≥ 20 h. For blends with low sulphur (<10 ppm) diesel fuel, oxidation stability can greatly decrease. It was recommended that any new blend, e.g., B10 in Europe will need to be standardized, with special emphasis on oxidation stability and validated carefully before release. The manufacturers' statement underlined the imperative for further research into biodiesel oxidation effects on FIE.

Although there are relatively few data available on the impact of biodiesel oxidation on the emissions from diesel engines [19], the effects of biodiesel oxidation on engine performance and emissions was studied by Monyem and Van Gerpen [14], where neat soybean-oil derived biodiesel was compared with No. 2 diesel fuel and a B20 blend thereof. Oxidized biodiesel samples were prepared by heating the biodiesel to 60 °C whilst bubbling through oxygen at a steady rate. After approximately 10 h, a Peroxide Value of 340 meq/kg indicated completion of oxidation. The fuels were tested in a turbocharged direct injection diesel engine run at constant rpm, for various engine loads and injection timings. All fuels reported similar thermal efficiency, though higher fuel consumption was noted for biodiesel—explained by its lower energy content. The heating value of oxidized biodiesel was relatively decreased by ~2.2%. Oxidized biodiesel produced significantly lower (~15% lower at full load) emissions of carbon monoxide (CO) and unburned hydrocarbons (HC) compared with unoxidized biodiesel, though no significant difference in oxides of nitrogen (NO_x) and smoke was observed. CO and HC results for No. 2 diesel were substantially higher than for both the biodiesels. Increased presence of oxygen in the biodiesel fuel, effectively produced a leaner fuel:air mixture, and this was a possible explanation cited although it was mentioned that inaccurate HC emission readings may have contributed. Shortened autoignition delay was also a possible factor as Cetane number increased with biodiesel oxidation, as shown in previous research. However both neat (oxidized and unoxidized) biodiesels produced 13–14% higher NO_x emissions than No. 2 diesel. No significant difference in NO_x was found between the No. 2 and B20 blends. Reduced Bosch smoke number was observed for the neat biodiesels and B20 blends, compared to No. 2 diesel with the oxidized biodiesel giving the largest reduction. The results of this study suggested that biodiesel oxidation can be at least partially beneficial in terms of exhaust gas emissions; since oxidized biodiesel showed reduced emissions of CO, HC and Bosch smoke number, although higher NO_x. Study of the effects of biodiesel oxidation on engine performance is limited, so that further studies appear needed in order to validate findings as well as to further explore oxidation effects.

Yamane et al. [54] studied the oxidation stability of biodiesel and its effects on combustion and emissions characteristics. The work comprised two studies; one examining the influence of FAME content on oxidation stability quality parameters, including peroxide value (PV), acid value (AV), kinematic viscosity (KV), and Rancimat induction period (RIP). The second study looked at the effect of biodiesel oxidation on diesel engine combustion and emissions character. In the introduction to the work the distinction was drawn between 'auto-oxidation' and 'thermal oxidation'; auto-oxidation being the oxidation process that occurs at normal temperatures when biodiesel is exposed to air, whilst thermal-oxidation is the accelerated process that occurs at much higher temperatures where the fuel is not necessarily exposed to air, but peroxides and oxygen dissolved in the fuel are important factors.

Engine fuel system problems that oxidation of biodiesel can cause were briefly discussed. Thermal oxidation of fuel in the tank may occur with hot fuel being returned unused from the engine injection system. Oxidation of fuel in the tank may cause fuel filter plugging by formation of polymeric oxidation products and corrosion of metal parts due to other oxidation products. Inside the fuel injection system, temperatures of 100–150 °C may be encountered; accelerating fuel thermal degradation, leading to high viscosity and fuel injector nozzle deposits. It was noted that few studies have reported the impact of oxidation products on engine performance and emissions and no research has yet been conducted to determine a maximum allowable degree of oxidation for the fuel to be used in diesel engines.

Three types of methyl ester were examined in the study: rapeseed oil methyl ester (RME), soyabean (SME), and linseed (LME), for which FAME compositions were measured and reported graphically. Approximate compositions are shown in Table 4. Simulation test equipment was used, comprising a common-rail fuel injection system in which fuel from a tank was pressurized by a radial piston pump to 20 MPa, receiving a thermal load and heating the fuel to 60 °C, before being pumped to a pressurized common-rail fuel gallery, from where fuel was injected at 1 Hz into a container at atmospheric pressure by an electronically controlled injector. Excess fuel bypassing the injector was returned to the fuel tank, and so too

Table 4
FAME compositions (%vol) of biodiesel fuel samples tested by[54].

Sample	Methyl palmitate (C16:0)	Methyl stearate (C18:0)	Methyl oleate (C18:1)	Methyl linoleate (C18:2)	Methyl linolenate (C18:3)	Other
RME	3	–	62	23	10	2
SME	10	2	20	58	10	–
LME	5	–	20	17	57	1

was the injected fuel. Only SME was tested in the simulated fuel system; PV, AV and KV were measured every 10 h or so over 250 h run time. Results showed AV and KV rose gradually over 250 h run time, while PV rose steeply at first then decreased. However, the resolution of the data was somewhat unclear so that the points at which AV and KV exceeded the limits defined by EN 14214 were not discernible. The results did indicate that significant degradation of fuel can indeed occur after prolonged circulation in the engine fuel system, although only after exceptionally long periods of run time. Results from further simulation studies might be useful for comparison, in particular to compare the behaviour of different FAMEs. However, such work may be of limited value given the clear limitations of simulation; in which the fuel does not experience 'real' conditions (i.e., the same temperature, pressure, flow rates etc.) as would occur in the fuel system of an actual running engine.

In Rancimat tests of the biodiesel samples (EN 14112 test conditions), RIP results for the LME, SME and RME were 2, 4 and 6 h, respectively. LME, with the highest amount of unsaturated methyl ester compounds was most easily oxidized. A 10 °C decrease in Rancimat test temperature was (again as in other work) shown to result in approximate doubling of RIP. Unusually though, when $T > 130$ °C for LME, then RIP unexpectedly increased. This was said to be due to the high temperature at which polymerization advanced before the formation of hydroperoxides. In other words, the rate of polymerization increased above the rate of hydroperoxide decomposition to volatile acids (detected by the Rancimat test) causing RIP to increase. Linseed oil (and thus LME) is well known for its high content of unsaturated esters and thus particular susceptibility to polymerization upon exposure to oxygen in air, where polymerization results in the hardening of the material. (Linseed oil is thus a traditional ingredient in oil paints, wood finishes and glazing putty where its polymerization upon exposure to air hardens upon application).

In other tests reported by Yamane et al. [54], PV, AV and KV of LME, SME, and RME were measured at ~30 min intervals, while fuel samples were held at 110 °C. Increases were seen in all three parameters in the order LME, SME, RME; AV and KV of SME and RME began to increase after around 6 h, while for LME increases occurred after only ~3 h. In all cases, PV was seen to increase significantly before rises in AV and KV occurred. In other words, peroxides accumulated as a precursor to polymerization and decomposition reactions, which resulted in respective increases in KV and AV (which were also shown to increase roughly in proportion). This behaviour is consistent with the accepted mechanism of oxidation (initiation, propagation and termination), where peroxide radical formation is the initial step in the process. As oxidation progressed in each of the samples, AV was seen to increase from ~0.5 to ~4 mg KOH/g, and KV was seen to more than double from the initial value ~5 mm^2/s at 30 °C. FAME composition was also measured for the samples as they underwent oxidation; the content of polyunsaturated linolenate and linoleate decreased with time (being consumed by oxidation), whilst the content of oleates and saturated stearate and palmitate relatively increased. Yamane et al. [54], reported that linolenic acid and linoleic acid have oxidation rates 25 and 12 times higher than that of oleic acid; these rates were also reported by Waynick [13]. Yamane et al. [54], suggested an inversely proportional relationship between RIP and the volumetric concentrations of oleate (18:1), linoleate (18:2) and linolenate (18:3):

$$\frac{1}{\mathrm{RIP}}\alpha[\mathrm{C18:1}]+12[\mathrm{C18:2}]+25[\mathrm{C18:3}] \tag{29}$$

However, these rates of oxidation would appear to disagree with values reported elsewhere. For example, relative rates of oxidation reported by Knothe are: 1 for oleates, 41 for linoleates, 98 for linolenates [5,7]. It would seem further investigation is called for to examine these parameters.

The RIP of SME blended with diesels fuels was also tested; examining low-sulphur content diesel (< 50 ppm) and another higher sulphur diesel (< 500 ppm). Results showed that RIP of the aggregate blend was reduced with the higher sulphur content fossil diesel; implying sulphur content affected antioxidant performance. Bannister et al. [19] also noted that when biodiesel is blended with petro-diesel, the sulphur content of the petro-diesel affects the oxidative stability of the blend. Sulphurous compounds behave as oxidation inhibitors and prevent formation of sludge and acids. Due to its lower polarity, ultra low sulphur diesel antagonises deposit and sludge formation. For the second part of the study by Yamane et al. [54] on engine emissions, a 20 l quantity of SME was deliberately oxidized by heating to 100 °C while air was bubbled through at 20 l/min. Two samples were treated this way; one sample for 12 h and the other for 24 h, producing one oxidized and another more heavily oxidized sample. Sample properties are noted in Table 5. The oxidized and un-oxidized fuels were then trialled in a single cylinder water-cooled direct injection (DI) diesel engine (NFD-170, Yanmar Co, Japan), where cylinder pressure, fuel injection pressure, nozzle needle lift were measured to calculate parameters such as rate of heat release. Exhaust emissions were also measured by FT-IR analyser, Bosch smoke meter and a particulate matter (PM) detection system incorporating measurement of soluble organic fraction (SOF). Results showed that as PV (degree of oxidation) of the test fuel increased, ignition delay decreased; effectively increasing Cetane Number (CN) of the fuel. Measurements of engine and emissions performance at fixed engine speed and injection timing (see Fig. 11) showed the start times of heat release for the oxidized fuels were several crank angle degrees earlier than the un-oxidized fuel. The oxidized fuels thus showed shorter ignition times; reducing the amount of pre-mixture formation, and a reduced *rate* of heat release during the initial combustion phase. As a result, the rate of pressure rise for the oxidized fuel was lower. However, NO_x emissions were clearly higher for the heavily oxidized fuel sample; (see Fig. 12) possibly indicating higher peak cylinder temperature. A possible explanation was increased cylinder pressure and temperature after top dead centre, due to the early onset of combustion and improved combustibility of the fuel owing to the long oxidation treatment. High temperature should also promote combustion of CO, and this was also clearly observed; the heavily oxidized fuel showed clearly lower CO emissions. Brake specific fuel consumption for

Table 5
Fuel sample properties of oxidized and un-oxidized fuels trialled in a diesel engine [54].

	Un-oxidized (fuel No. 1)	Oxidized (fuel No. 2)	Heavily oxidized (fuel No. 3)
Treatment time (h)	0	12	24
PV (meq/kg)	18	567	760
KV (mm^2/s@30 °C)	5.2	6.4	11.2
AV (mg/KOH/g)	0	1	3.5

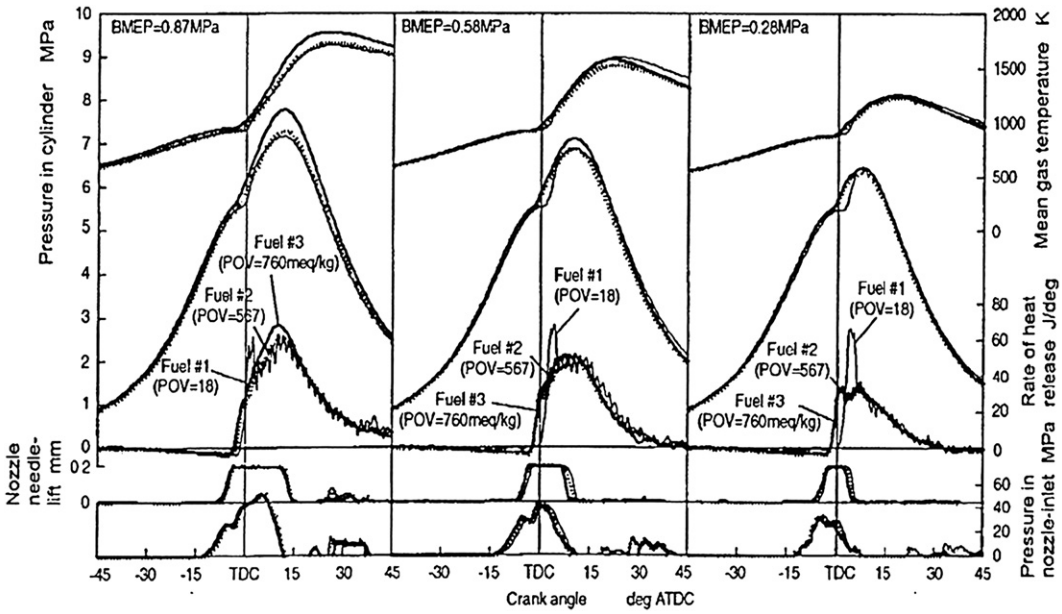


Fig. 11. Crank angle history of in-cylinder temperature, pressure, rate of heat release, needle lift and injection pressure [54].

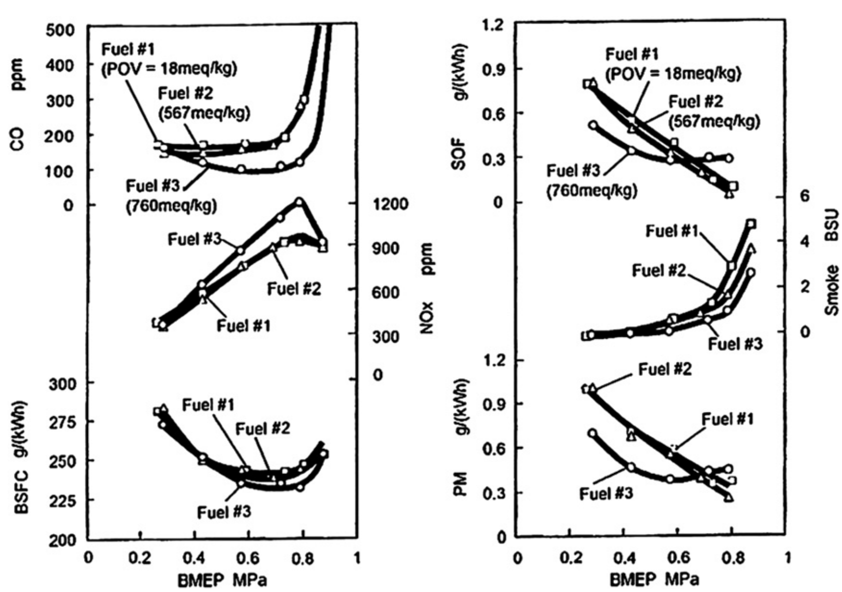


Fig. 12. Fuel consumption and emissions characteristics of oxidised (2, 3) and un-oxidised (1) biodiesel fuel [54].

the heavily oxidized fuel was relatively lower. Smoke density was somewhat decreased with the oxidized fuels, possibly indicating improved combustion efficiency. PM and SOF were also lower for the oxidized fuels at low load, however this was reversed at high load. This change was probably due to the increased amount of hydroperoxide polymers with high boiling points present in the heavily oxidized fuel, which may increase PM and the soluble organic fraction at high load.

The authors explained that generally, higher viscosity diesel fuel yields a larger droplet size in the fuel spray, which decreases combustion rate and increases unburned hydrocarbon emissions, due to poorer fuel/air mixing. However, the results reported by Yamane et al. [54] showed that despite its higher viscosity, oxidized biodiesel can present improved combustion results; suggesting that the chemical properties of the fuel (presence of hydroperoxides and organic acids), surpasses the negative effects due to high viscosity and poor spray formation.

The present author carried out an experimental investigation of factors affecting biodiesel engine performance and exhaust emissions [55], where a range of biodiesel fuels were tested: 7 different FAME fuels and 5 ethyl esters from various vegetable oils and two animal fats. Identical aliquots of rapeseed FAME were also contaminated with (i) vegetable oil, (ii) water, and (iii) high levels of TBHQ antioxidant; another was deliberately oxidized. Fuels were tested in a 50 bhp engine equipped with a dynamometer and exhaust emissions analyser measuring CO (%vol), CO_2 (%vol), O_2 (%vol) and NO_x (ppm) at different engine load points, with petro-diesel as a benchmark fuel. Results indicated levels of oxygen in the exhaust emissions were increased when running biodiesel, compared to data for petro-diesel. At the highest engine load point, levels of biodiesel CO were 43% lower. No differences in CO_2 levels were obvious between any of the fuels. Levels of biodiesel NO_x were either: slightly higher than, similar to, or lower than levels recorded for petro-diesel, where increased

biodiesel unsaturation level correlated with higher NO_x levels. Relevant to the discussion here; oxidation of biodiesel caused the most obvious difference in emissions, which resulted in relatively higher exhaust levels of oxygen and lower CO. Oxidized fuel also recorded noticeably lower NO_x levels, in contrast to results of literature studies discussed above (which observed similar and increased NO_x levels for oxidised biodiesel fuel). Biodiesel oxidation was thus observed to be an important factor causing variation in emissions levels, as reported elsewhere in the literature. Contaminants (vegetable oil, TBHQ, water) had little effect on engine performance or emissions. A wider study of the performance of oxidised (and contaminated) biodiesel in different designs of engine is called for in order to further investigate these effects.

Deutz, a leading engine manufacturer [56] in 2009 published general recommendations on use of biodiesel in their engines, newly permitting the use of 100% biodiesel in a wide range of their engine models. However, "users of biodiesel in DEUTZ engines [were recommended to] choose their [fuel] suppliers very carefully and have them guarantee compliance with the limit values specified by EN 14214". The publication stated that relative to petro-diesel, "in operation with biodiesel… particulate emission is reduced considerably by approx. 20 to 50% and the soot emission by approx. 40 to 60%. The carbon monoxide emissions and hydrocarbons are reduced by up to 25% or 50%. The emission of nitrogen oxides (NO_x), on the other hand, rises by approx 10%", i.e., the emissions performance of biodiesel leads to a clear general improvement over petro-diesel, with the exception of NO_x.

However, "poor evaporation capacity [volatility] of biodiesel in comparison with diesel fuel can lead to an increased infiltration of fuel into the engine oil. If the amount of biodiesel infiltration is too high, polymerisation, subsequent clogging of the engine and failure of the engine lubrication with serious engine damage can occur. Biodiesel infiltration is especially critical in the low load range. Therefore the lubricating oil change interval must be halved in relation to operation with diesel fuel in accordance with EN 590." A key impact of biodiesel oxidation is evidently on engine oil performance, requiring a shorter oil-change interval. "Another problem is possible fuel filter blockages", however not attributed to the oxidation of biodiesel in the fuel system, but "due to dissolving of deposits [accumulated during use of petro-diesel] after changing over from diesel fuel to biodiesel. This is recognisable by a marked reduction in performance after the changeover. The problem can be remedied permanently, however, by changing the filter once; this must be done approx. 30 to 50 h after the first changeover." The solvent properties of biodiesel can dissolve residual deposits and sediments (effectively washing the fuel system) which can then block fuel filters, i.e., biodiesel acting as a solvent, rather than its degradation by oxidation, is likely the true cause of many reported fuel filter blockages linked to biodiesel use. Further, it was recommended that "longer standstills of more than 4 to 6 weeks with biodiesel are to be avoided (e.g., the winter break in agriculturally used machinery) because deposits can form on the injection system and the plungers and the engine can no longer be started in the worst case. Instead, the engine should be operated and shut down with diesel fuel before the break." Oxidative degradation is then recognised as a clear problem for engines left idle with biodiesel fuel in the system, though flushing through with petro-diesel prior to any idle period, is offered as a straightforward solution.

Bannister et al. [19] noted that compared to petro-diesel, biodiesel generally has greater surface tension, viscosity, density and is less volatile; hence biodiesel use can lead to an increase in the mean droplet size of the injected fuel spray. Larger droplets can result in more spray impingement on cylinder walls and can cause an increased amount of biodiesel to collect within the engine sump oil. Being less volatile than petro-diesel, less collected biodiesel evaporates from the oil leading to greater accumulation in the engine oil. Oxidative degradation can then cause significant increase in engine oil viscosity, resulting in loss of engine performance and increased fuel consumption (due to increased friction), increased engine wear and can necessitate a premature oil change. Oxidation can lead to solid deposit (or soot) formation within the fuel or lubricant systems reducing engine durability. Soot formed can lead to increase in component wear due to abrasion. In extreme cases, oil starvation could occur due to filter clogging and blocked oil channels.

4.1. Remaining challenges and unanswered questions

The chemistry of biodiesel oxidation is reasonably well understood as outlined above, though establishing clear links between stability test measurements (e.g., RIP) and real world performance of biodiesel in engines; enabling confident predictions of biodiesel performance based upon fuel property character remains a challenge for the biodiesel research community to address. Waynick [13] commented to this effect, stating that "although the exact details of how the chemistry of biodiesel fuel impacts stability properties has not yet been determined, a reasonably clear level of understanding does now exist… Linking the understanding of biodiesel fuel stability with equipment performance characteristics is the one area of work that now needs to be accomplished to advance biodiesel usage… There is a lack of engine equipment test results, making it impossible to link existing understanding of biodiesel chemistry to the real world". Similarly, McCormick et al. [9] recommended "additional testing of real equipment to verify the results of storage stability tests using standard methods". The authors commented that "unfortunately there is no standard engine test to assess the impact of fuel stability on fuel system durability and injector deposit formation, so that testing of biodiesel and its blends of varying stability in real fuel systems is required." Without test data that facilitates comparison, it is very difficult to predict the impact of biodiesel instability on fuel system durability and injector deposit formation. Evidently, further studies of the impact of biodiesel oxidation on diesel engine equipment are needed in order to gather such data.

The European biodiesel standard EN 14214, requires >6 h oxidation stability according to EN 14112 test method. This method was formally added to the ASTM D 6751 biodiesel specification in the United States in 2006 [1]. However, ASTM D 6751 is more lenient; requiring only >3 h by the same method [25]. How oxidatively stable does biodiesel need to be to prevent problems? Inconsistency between European and American fuel quality standards suggests the answer to this question is not settled.

In his 2005 paper, Westbrook [6] pointed out that the vast majority of U.S. biodiesel RIP ranged between 1–4 h; so that excessive amounts of antioxidants would be required to meet the European specification. Westbrook commented that "to date there has been no controlled study of the minimum induction period required to minimize the chance of problems in the field. Many in the industry point to the lack of reported problems, linked to unstable biodiesel, as proof that U.S. fuels are for the most part acceptably stable. As such, it is expected that any ASTM specification that uses the Rancimat will probably have a lower minimum induction period, perhaps 4 h rather than 6." [6].

It is well documented that the oxidation of biodiesel could be the cause of engine problems; warranting inclusion of a target value for oxidation stability (RIP) in fuel specifications. The chances of engine problems arising in the field should thus be reduced if the target is met. However it seems evidence is lacking, at least in the open literature, which might support any precise

specification value for oxidation stability (h), characterized by the Rancimat method—consequently the result has reduced meaning in terms of quantifying the risk of developing engine problems. The EN 14214 specification on oxidation stability requiring >6 h RIP may be adequate, or too lenient. There appears to be a lack of evidence that would enable arrival at either conclusion. The absence of such evidence may undermine the importance of a fuel specification for oxidation stability. There is then, a clear need for further study of this issue with the aim of gathering supporting evidence. However, an increase of the limit to 8 h is approved for the next version of EN14214 [21,31]. The study by Karavakalis [31] (see Section 3.7) observed that the relative stability (RIP) measured for a range of neat biodiesels was altered when blended with petro-diesel; dependent on the origin/composition of the petro-diesel. This presents a further complication, and suggests RIP measured for neat biodiesel is less relevant if it is to be blended with petro-diesel.

Biodiesel oxidative deterioration can take place in the fuel supply chain, but also it is noted, in the vehicle fuel system itself [10]. The severity of oxidizing conditions experienced by fuel circulating in a particular engine fuel system will vary according to the system and fuel tank design—circulation temperatures and flow rates will be significant factors. Older engines, equipped with lower pressure injection systems may be more tolerant to lower stability fuel than modern engines that utilize much higher injection pressures. Circulating fuel is heated as it travels through the fuel system. Biodiesel *thermal* stability may well be important at the relatively higher temperatures encountered. Thermal polymerization of esters becomes important when temperatures of 250–300 °C are reached. It may be the case that oxidative degradation of biodiesel proceeds as the fuel circulates in the engine fuel system, where hot fuel is returned unused to the fuel tank. Certain engine types and or warmer climates might require higher stability fuel. Over the engine runtime, fuel quality could deteriorate by autoxidation and or *thermal* polymerization. Circulating fuel would experience a thermal heating cycle dependent on factors such as run time, ambient temperature, the level of fuel in the tank and general fuel system design. Fuel tank contents can be agitated within a vehicle in motion; promoting exposure of the fuel to air. Keeping the fuel tank topped up might help delay fuel degradation. For vehicles kept in storage or for those used only periodically, deterioration in quality of the fuel stored in the tank may be a more significant issue, especially in warmer climates. However, low stability fuel may not pose a problem so long as the fuel is consumed reasonably quickly. Such concerns over biodiesel fuel quality must be addressed for market acceptance. In this context it appears that further investigation of the performance of biodiesel in vehicle fuel systems is needed.

5. Conclusions from the literature survey on oxidation stability

1. Biodiesel fuel properties can deteriorate during storage and in use by autoxidation. Critical fuel properties such as Cetane number and viscosity are altered, engine exhaust emissions are affected and diesel engine operational problems can result caused by the accumulation of deposits, varnishes and sediments on engine parts—promoting corrosion and or impairing component operation. Oxidation products can attack elastomers, clog fuel filters and contaminate engine lubricating oil. Corrosive acids and deposits may cause increased engine wear. Blending biodiesel with petro-diesel can exacerbate insoluble formation.
2. The susceptibility of biodiesel to autoxidation is fundamentally due to fatty acid chain unsaturation. Di- and tri- unsaturated fatty acids contain the most reactive bis-allylic sites for initiating autoxidation. Their increased presence disproportionately reduces oxidation stability of biodiesel.
3. The standard method (defined by EN 14214) for biodiesel oxidation stability measurement uses a Rancimat instrument, giving an Induction Period result (h). However the Rancimat method suffers disadvantages; being time consuming to perform as well as significant uncertainty/imprecision of the result. A range of other techniques can also be used for stability characterization. Alternative techniques such as spectrofluorimetry (discussed in Section 2.2.1) may potentially supersede Rancimat.
4. Biodiesel oxidation stability is affected by FA composition, specifically by the degree of fatty acid unsaturation. Also impurities such as metals, FFAs, additives and antioxidants strongly affect stability. Physical conditions of the Rancimat test, such as sample mass and viscosity, and pro-oxidising conditions (air flow, temperature) clearly affect the measurement.
5. Oxidation of biodiesel can only be delayed and not completely prevented. Delaying techniques include control of FA composition, impurities, storage conditions and antioxidant dosing.
6. The effects of biodiesel oxidation on diesel engine equipment are reported by relatively few authors. Establishing clear links between stability test measurements and real world performance of biodiesel in engines remains a research challenge to address. It appears agreement has not yet been reached over the acceptable minimum biodiesel oxidation stability necessary to prevent engine problems.

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